SURFACTANT SCREENING TO ALTER THE WETTABILITY AND AID IN ACIDIZING CARBONATE FORMATIONS

A Thesis

by

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ABSTRACT

Surfactant flooding in carbonate matrix acidizing treatment has been widely used for changing the wettability of the rock and to achieve low IFT values. Optimizing the type of surfactant and concentration for the specific oil field is very important in order to avoid formation damage and to reduce the treatment cost.

We built an experimental procedure for screening the right surfactant to alter the wettability and aid in acidizing of Pekisko formation, Canada, which is strongly oil-wet and has high viscosity oil. Five surfactants were tested out of which three are cationic, one amphoteric and the other one was a fluoro-surfactant. Measurements were made of interfacial tension with different surfactant types/concentrations in brine with the oil and xylene, critical micelle concentration of each surfactant, solubility characteristics of the surfactants, compatibility of the chemical additives, wettability of the core after treating with surfactants, and core flooding in the laboratory to simulate matrix acidizing.

From the results obtained we noted that the fluoro-surfactant can cause formation damage due to precipitation in the brine. So the compatibility of every chemical additive should be tested first. The use of xylene as a pre-flush solution lowered the CMC and hence reduced the cost of the surfactant treatment. Aromox, an amine based surfactant was best suited for matrix acidizing treatment of the Pekisko formation.

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1. INTRODUCTION AND LITERATURE REVIEW

For the carbonate reservoirs, matrix acidizing is an effective way to remove the formation damage caused by drilling mud invasion, clay migration, clay swelling and inorganic scaling. The purpose of matrix acidizing is to reduce the skin factor which is achieved by forming wormholes or pathways, from several inches to a few feet long, to improve the production of crude oil. In matrix acidizing the treatment fluid is pumped below fracturing rate and pressure as opposed to hydraulic fracturing.

1.1 Carbonate Matrix Acidizing

1.1.1 History

Carbonate matrix acidizing was started more than 100 years ago. In 1895, Ohio Oil Company performed limestone matrix acidizing using hydrochloric acid (HCl). The technique was recorded in 1896 (Williams et al. 1979) and it increased the oil production by three times but the well casing was severely corroded by the strong acid. Due to this the technique did not gain much popularity in the following 30-40 years.

In 1931, Dr. John Grebe of the Dow Chemical Company discovered that arsenic had a chemical inhibition capacity of HCl on metal. A year later, Michigan based Pure Oil Company pumped HCl mixed with arsenic as a corrosion inhibitor provided by Dow Chemical Company into a limestone formation (Williams et al. 1979). It increased the

oil production from 0 to 16 bbl/day. In the following years several commercial acidizing services were established due to this success. To improve the effectiveness of the treatment, several acid additives including surfactants, corrosion inhibitors, intensifiers, fluid loss additives, and so on started to be used (Chilingar et al. 1989).

1.1.2 Theoretical Production Enhancement

Matrix acid treatments are conducted in damaged wells which have near wellbore flow obstruction. Fig. 1 shows a radial production system in which the radius of the wellbore is r_w and the damage exists from r_w to r_s. The permeability of damaged zone is k_s which is less than the permeability k of the undamaged zone extending from r_s to r_e.

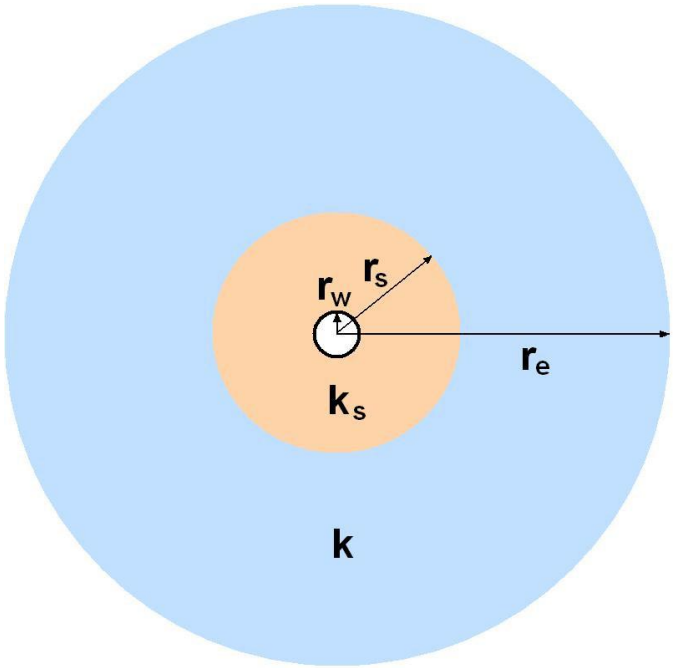

Fig. 1: Schematic of the damaged zone of a radial production system

In the present system, the ratio of the productivity indices of undamaged and damaged zones is given by Eq. 1:

$$\frac{Js}{J} = \frac{(ks/k)\log(re/rw)}{\log(rs/rw)+(ks/k)\log(re/rs)} \tag{1}$$

Where J_s is the productivity of the damaged formation and J is that of the undamaged formation. Fig. 2 shows the productivity enhancement caused by increasing the permeability of the damaged zone by matrix acidizing treatment.

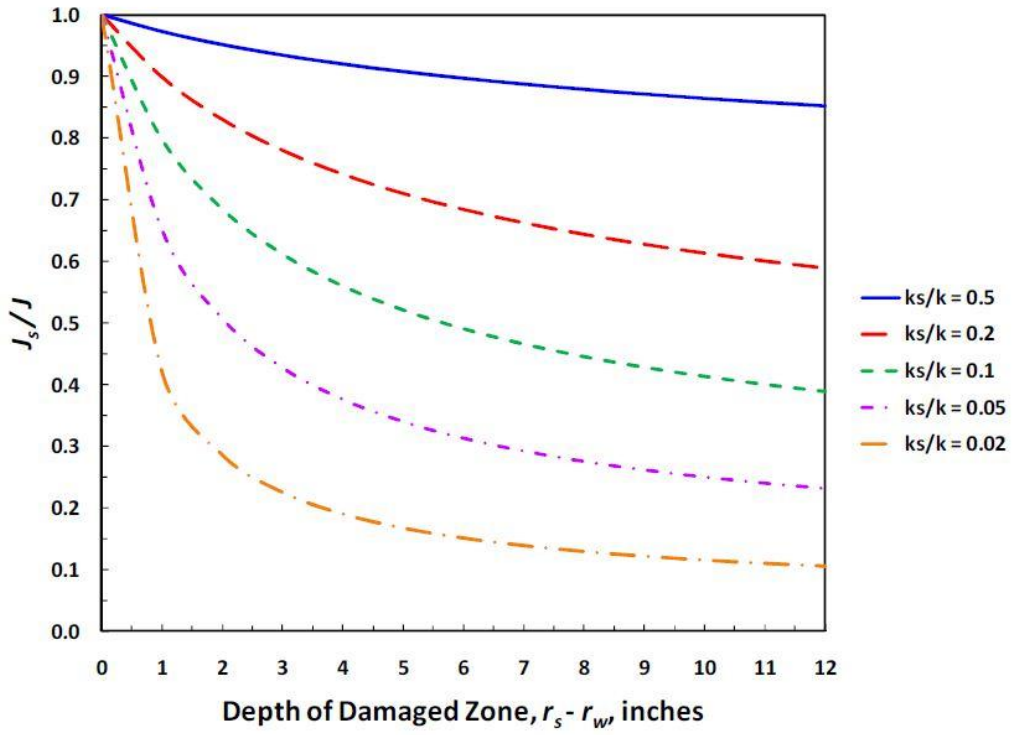

Fig. 2: Production enhancement by increasing damaged zone permeability (Yu 2011)

1.1.3 Chemistry of Carbonate Matrix Acidizing

Carbonates occur naturally as sediments and reefs in modern tropical and temperate oceans, as ancient rocks, and as economically important mineral deposits. The most common carbonate minerals are calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$).

Hydrochloric acid is commonly used in carbonate acidizing. However, if the temperature is high then corrosion becomes an issue and less corrosive organic acids, such as acetic or formic acids are used.

HCl dissolves the calcite and dolomite present in the carbonate rocks by the following reactions:

$$CaCO_3 + 2\ HCl \rightarrow CaCl_2 + CO_2 + H_2O \quad (2)$$

$$CaMg(CO_3)_2 + 4\ HCl \rightarrow CaCl_2 + MgCl_2 + 2\ CO_2 + 2\ H_2O \quad (3)$$

The rate of dissolution of calcite is determined by the rate at which the acid is pumped into the formation. Reaction of acid with the rock creates channels or wormholes which bypass the damaged zone and hence, increase the production of oil (Economides et al. 1994).

Hydrochloric acid is the most commonly used acid in carbonate matrix acidizing. Generally 15 wt% HCl in water is used; higher concentrations of the acid can be used with more effective corrosion inhibitors. The main advantages of using HCl are that it's

cost effective and the reaction products obtained with carbonate rocks, namely calcium chloride and magnesium chloride, are both soluble in spent acid. The disadvantage of HCl is that it causes corrosion of well tubulars and pumps at temperatures greater than 250^{o} F.

Organic acids such as formic acid (HCOOH) and acetic acid (CH_3COOH) are also used in carbonate matrix acidizing because they are weaker acids compared to HCl and hence, cause fewer corrosion problems. 10 wt% solutions in water is the commonly available form of acetic acid in the market. Its reaction products with carbonate rocks are calcium acetate ($CaOOCCH_3$) and magnesium acetate ($MgOOCCH_3$) and they are usually soluble in spent acid. Acetic acid is more expensive than either hydrochloric acid or formic acid based on the cost per unit of dissolving power. Formic acid is cheaper but it is more corrosive compared to acetic acid and more difficult to control in the presence of acid sensitive metals, such as aluminum or chromium. However, formic acid can be used at temperatures up to 400^{o}F with the help of effective inhibitors (Williams et al. 1979).

Recently, dicarboxylic acids or their mixtures, known as high temperature organic acids (HTO acids), have been found to be useful in acidizing subterranean formations at temperatures up to 400^{o}F. Some of these acids are oxalic acid, malonic acid, pimelic acid, succinic acid, glutaric acid, adipic acid and their mixtures. In addition to creating wormholes in carbonate formations, HTO acids can remove carbonate scale at high temperatures and cause very low corrosion to the tubing and casing.

1.2 Role of Surfactants in Acidizing

1.2.1 Definition of Surfactants and Their Properties

"Surfactants" is an abbreviation for "surface active agents", which literally means active at a surface. The surface can be between solid and liquid, between air and liquid, or between a liquid and a different immiscible, liquid. Surfactants have some special characteristics and they are: adsorption; micelles; solubility; solubilisation; micro emulsions; wetting; foaming and defoaming; macro emulsions; dispersion and aggregation of solids; and detergency.

A surfactant can adsorb on the surface because there are two groups in the molecule, Fig. 3: a hydrophobic (water-hating) group and a hydrophilic (water-liking) group.

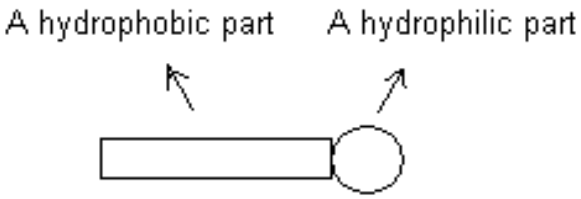

Fig. 3: The basic structure of a surfactant

There are two opposing forces of interaction between the surfactant molecules (Porter, 1994). One is the repulsive force between the polar groups in water. This has been shown in Fig. 4. The larger this charge, the greater the repulsion and lesser tendency to form micelles. Another force is between the hydrophobic groups if there is a bond attracting them together. The reason for this is complex and due to enthalpy and entropy

changes when the alkyl group is transferred from a hydrocarbon environment to solution in water.

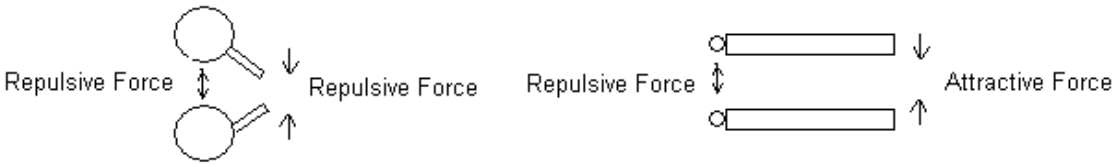

Fig. 4: Forces between surfactants

When the molecules are very far apart, both of these two forces are very weak. The two interactions will increase if the concentration increases. The molecules probably cannot aggregate if the repulsive force is much greater than the attractive force. The surfactant molecules will remain monodispersed in solution at high concentration. This is the situation when the surfactant is very soluble, due to the hydrophobic effect being very weak. On the other hand, the molecules will aggregate together if the attractive force is much stronger. This is the situation when the molecule is partially soluble because of the large size of hydrophobic group. The relative strength of repulsive and attractive forces determines Critical Micelle Concentration (CMC, will be defined later). In comparison of the two surfactants, the one with larger hydrophobic effect will have a lower CMC than the other(Li 2011).

The adsorption of a surfactant from the solution onto a surface depends on the concentration as shown in Fig. 5 (Porter 1994).

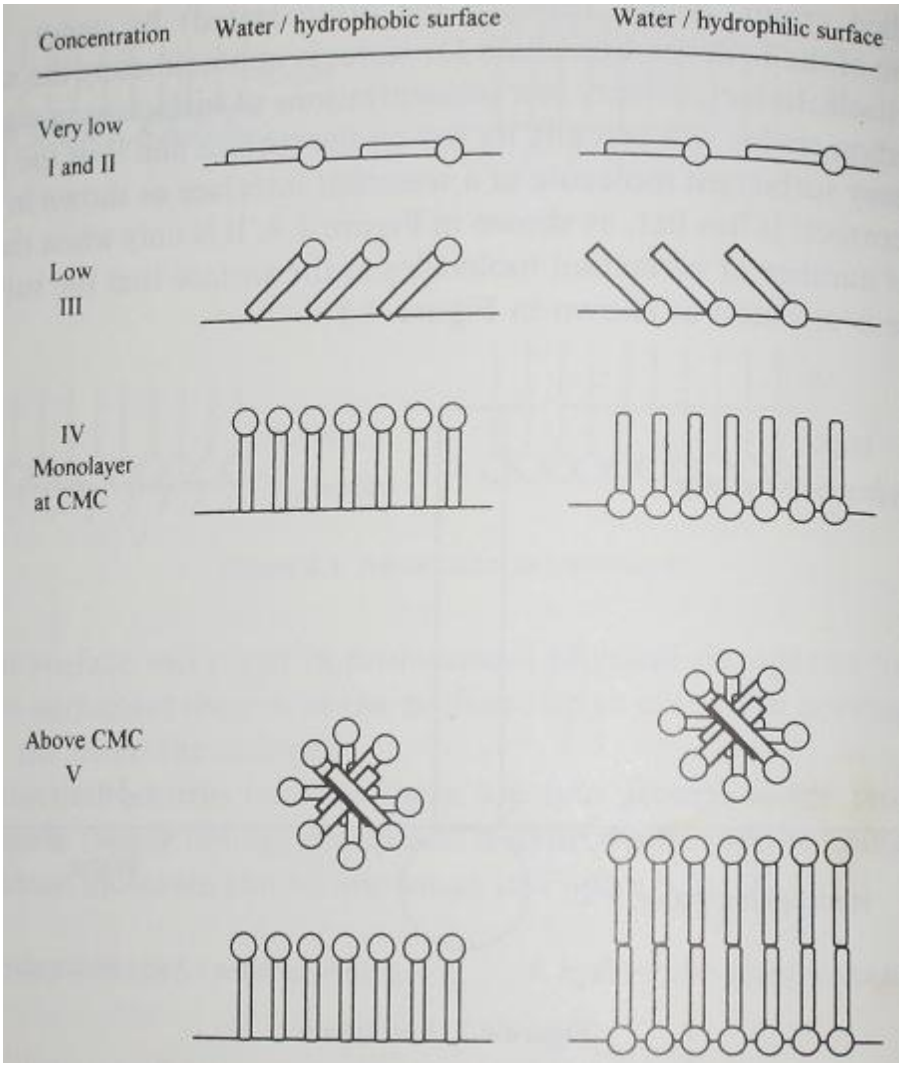

Fig. 5: Adsorption of surfactants (Porter, 1994)

At very low concentrations (I and II), there is no orientation and surfactant molecules lie on the surface. At stage III, the concentration increases and the number of molecules increases, there is not enough room for all the molecules to lie on the surface, so they are orientated in a way. At concentration IV, the number of molecules is large enough to form a monolayer, and this particular concentration is called Critical Micelle

Concentration (CMC). Once the concentration is above CMC (V), more than one layer of surfactant molecules can form ordered structures on the hydrophilic surfaces.

1.2.2 Surfactant Classification

Based on the chemical structures of the hydrophilic group, surfactants can be classified as:

Anionic - carrying a negative charge

Nonionic - carrying no charge

Cationic - carrying a positive charge

Amphoteric - carrying a positive or a negative charge or both

1.2.3 Surfactant use in Acid Stimulation

Surfactants are used in acidizing treatments to do one or more following functions: water wet the formation, break emulsions or sludges, reduce surface or interfacial tension, remove fine particles, form foams for acid diversion and prepare emulsified acids for deep acid penetration.

Imbibition is described as a process by which a wetting fluid is drawn into a porous medium by capillary action (Høgnesen et al. 2004). Spontaneous imbibition of water is an important improved oil recovery technique (Morrow and Mason 2001). Unfortunately about 90 % of the carbonate reservoirs are neutral to oil-wet so spontaneous imbibition of water is unlikely to occur. So wettability alteration of the rock surface is essential for

the water to imbibe into the formation, in other words wettability alteration is necessary to overcome the capillary barrier and for the water to enter the low permeable formations. Wettability alteration towards more water-wet conditions can be obtained through the use of surfactants (Standnes and Austad 2000; Standnes et al. 2002).

Understanding the mechanism of surfactant is crucial in selection application (Bortolotti et al. 2010). (Chen et al. 2001) checked the ability of nonionic and anionic surfactants to alter the wetting characteristics of rocks to less oil-wet conditions. (Standnes and Austad 2000) examined the spontaneous imbibition of different surfactants into oil-wet chalk and found that cationic surfactants alter the rock wettability to a more water-wet state by desorbing organic carboxylates from the rock surface. Austad et al. (Standnes and Austad 2003; Strand et al. 2003) suggested that cationic surfactants performed better than anionic surfactants in changing the rock wettability to a more water-wet state.

For cationic surfactants, the mechanism responsible for altering the wettability of oil-wet carbonate rock is the formation of ion pairs between the cationic heads of the surfactant molecules and the acidic component of crude oil adsorbed on the rock surface. The ion-pair formation was able to strip the adsorbed layer of crude oil components off the rock surface, exposing carbonate rock that was originally water-wet. In contrast, anionic surfactant molecules form a monolayer on the surface of carbonate rock through the hydrophobic interaction of the tails of the surfactant molecules with the adsorbed crude oil components on the rock surface. The hydrophobic interactions are much weaker than

the ion-pair interactions, which could potentially explain why cationic surfactants performed better than the anionic surfactants in altering the wettability of the carbonate rock to a more water-wet state. (Salehi et al. 2008) showed that ion-pair formation between the charged head groups of surfactant molecules and the adsorbed crude oil components on rock surface was more effective than the adsorption of surfactant molecules as a monolayer on the rock surface in changing the rock wettability to a more water-wet state.

2. PRELIMINARY ANALYSIS

We received two core samples and an oil sample from Pace Oil and Gas Ltd., Canada. They were taken from the Pekisko formation, Canada.

2.1 Core Samples

The core samples were tested for homogeneity and composition.

2.1.1 Using Computerized Axial Tomography (CT scan) to Test the Homogeneity of the Cores

We conducted a CT scan of the core samples to check their homogeneity. Twenty images at different cross-section lengths were taken for each core and the images were analyzed to see the presence of vugs. We noted that the cores were fairly homogeneous without any cavities. It should be noted that the presence of a cavity will be clearly shown in the image with a distinct red or blue color. The images of samples are shown in **Appendix A.**

2.1.2 Using X-Ray Fluorescence (XRF) to Test the Composition of the Cores

We conducted XRF of all the core samples to find out their composition. The main component of each core was calcium carbonate (about 95 %). The cores were identified as limestone. The percentage of individual elements present is shown in **Appendix B**.

2.1.3 Using X-Ray Diffraction (XRD) to Test the Crystal Structure of the Molecules

XRD was conducted to determine the crystal structure of the molecules present. Data was collected on a Bruker D8 Advance powder X-ray diffractometer (CuKα, LynxEYE detector, Bragg Brentano geometry) with a zero background sample holder. The result of the experiment has been shown in Fig. 6.

Based on the results it was determined that the pattern corresponds to calcite and/or substituted calcite phases. Exact composition could be established only from other physicochemical methods.

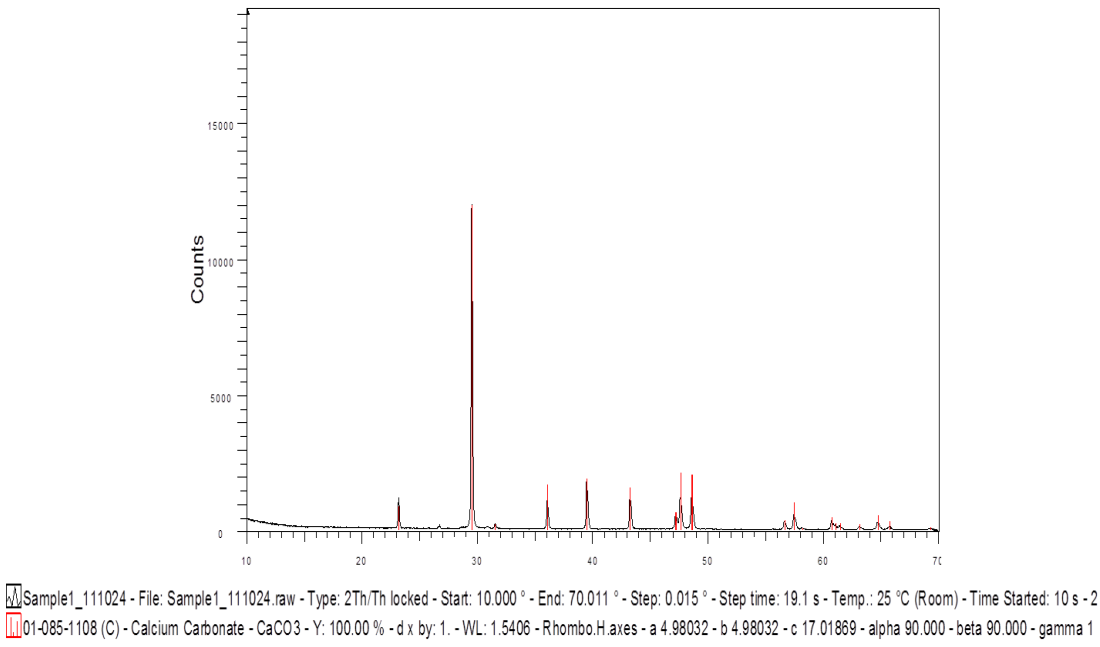

Fig. 6: The crystal structure of the molecules of the cores sample

2.2 Oil Sample

Oil sample was tested for their acid content, asphaltene content and composition.

2.2.1 Gas Chromatography – Mass Spectrometry (GC-MS)

GC-MS was conducted on the oil sample received to find out the individual components and their percentages present in the oil. The sample named 13-25-101-5 consists of 37 % of aromatic hydrocarbons and 63 % of aliphatic hydrocarbons. The individual components of each sample have been listed in **Appendix C**.

2.2.2 Oil Viscosity Measurement

Viscosity of the oil sample was measured using the Glass Capillary viscometer. The experiment was repeated 3 times to make sure the value obtained was correct. These values have been shown in Table 1. We obtained kinematic viscosity using this method; the value was then multiplied by oil density to obtain dynamic viscosity.

Table 1: Viscosity of oil sample 13-25-101-5

Trial	Viscosity (cp)
1	39.1
2	38.2
3	38.2

So the viscosity of the oil was found to be 38.2 cp at 30 ^{o}C.

2.2.3 TAN and TBN Measurements

907 Titrando was conducted on the two oil samples received to find out the individual TAN and TBN.

TAN: Total acid number means potassium hydroxide in mg required to neutralize total acid components in 1g of petroleum products. Solvent: 500 mL toluene + 495 mL IPA + 5 mL H_2O.

TAN of oil sample 13-125-101-5 was found to be 0.4 mg KOH/g.

TBN: Total base number which is a measure of the level of BASE in the oil and is determined by measuring the amount of HCl in mg taken to neutralize the base reserve in 1 gram of oil. Solvent: Toluene: glacial acetic acid = 1 : 1 (volume ratio).

TBN of oil sample 13-125-101-5 was found to be 2.62 mg HCl/g The reports of the two experiments are shown in the **APPENDIX C**.

3. INTERFACIAL TENSION MEASUREMENTS

3.1 Surfactants to Reduce Interfacial Tension

For gas wells in low permeability reservoirs, accumulation of the aqueous phase near the wellbore formation rock, known as water blockage and shown in Fig. 7, will reduce the relative permeability to gas and gas production (Bennion et al. 1996). Therefore, low surface tension is required to reduce capillary force that traps the aqueous phase in the pore throat.

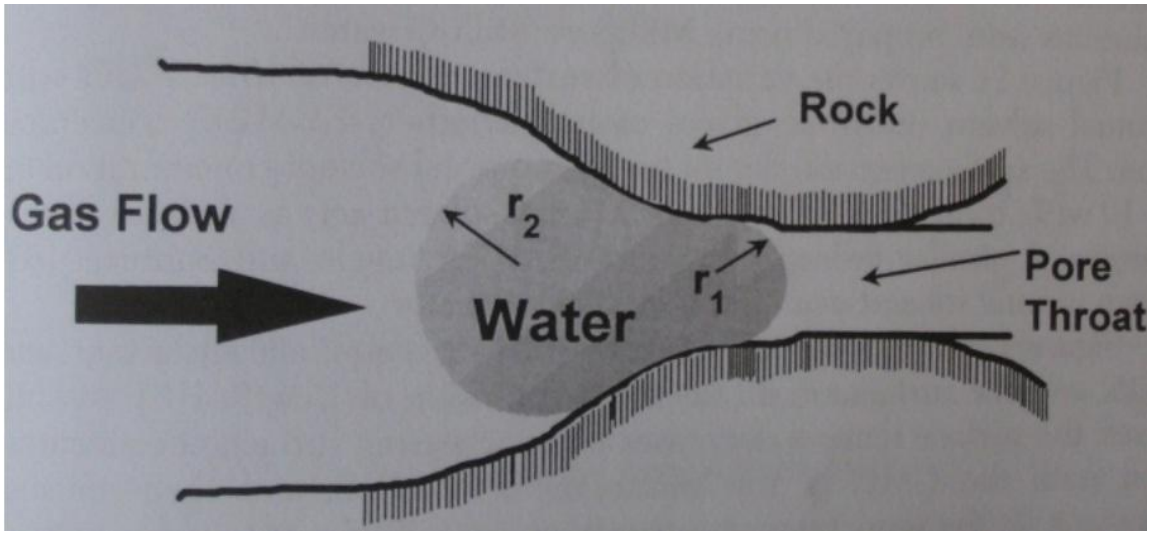

Fig. 7: Water blockage in gas reservoirs (Schramm 2000)

The pressure drop required to mobilize a drop of trapped spent acid can be expressed as

$$\Delta p = 2\sigma(\frac{1}{r_1} - \frac{1}{r_2}) \quad (4)$$

where σ is the surface tension, *r1* and *r2* are the radius of the water droplet. To reduce the capillary force, one way is to lower surface tension and it can be achieved by the addition of surfactants. (Dabbousi et al. 1999) reported that surface tension is a function of acid type, concentration, ionic strength and additive type and concentration (1999). The addition of surfactants to a strong acid reduces its surface tension until critical micelle concentration CMC, after that, the surface tension does not change much if surfactant concentration is increased (Fig. 8).

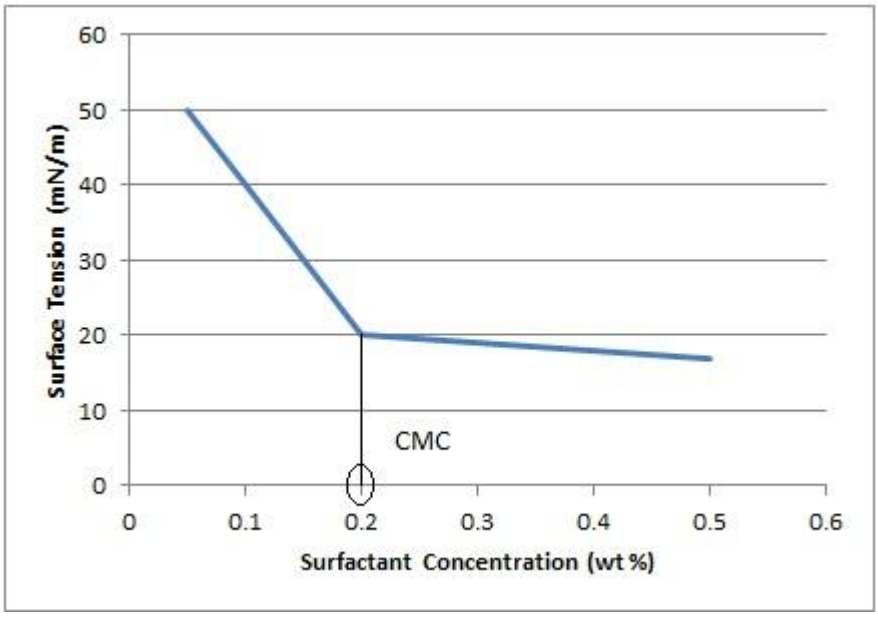

Fig. 8: Surface tension changes with surfactant concentration

Imbibition is defined as the displacement of one fluid (non-wetting) by another immiscible fluid (wetting). Water imbibition is the process by which water flows into the porous media by capillary forces. These forces allow the water to enter the tiny pores and displace the oil present inside them. But water imbibition is not a spontaneous process because of the high IFT values between oil and water. A surfactant present in the solution reduces the surface forces or IFT between water and oil and facilitates the imbibition process (Al-Lawati and Saleh 1996).

3.2 Experimental Studies and Results

The interfacial tension (IFT) was measured on Kruss Easydyne tensiometer. The Pekisko formation is a shallow reservoir with an average temperature of 28^{o}C and the reservoir pressure is just a few hundred psis, so the IFT measurements were conducted at room temperature and pressure. In the following pages the terms lighter phase and heavier phase have been used to refer to the hydrocarbon phase and aqueous surfactant phase respectively.

The first set of measurements we conducted was the variation of interfacial tension (IFT) between oil and surfactant solutions in DI water with surfactant concentration. We noted that the CMC of each of these surfactants was about 0.2 wt% or 2000 ppm. Table 2 shows the IFT values for different surfactants and Fig. 9 shows a plot of these values.

Lighter phase: **Oil 13-25-101-5**

Heavier phase: **Surfactant solution in DI water**

Table 2: Values of surface tension for different surfactant concentrations between oil and surfactant solutions in DI water

Surfactant	PF-AT	SS 918	Aromox C/12	Arquad	Ethoquad
Surf.Conc. (wt%)	IFT (mN/m)	IFT (mN/m)	IFT (mN/m)	IFT (mN/m)	IFT (mN/m)
0.1	8.4	5.5	4.7	6.3	15.8
0.2	4.4	4.8	4.1	5.9	12.6
0.5	3.3	3.9	3.8	5.6	11

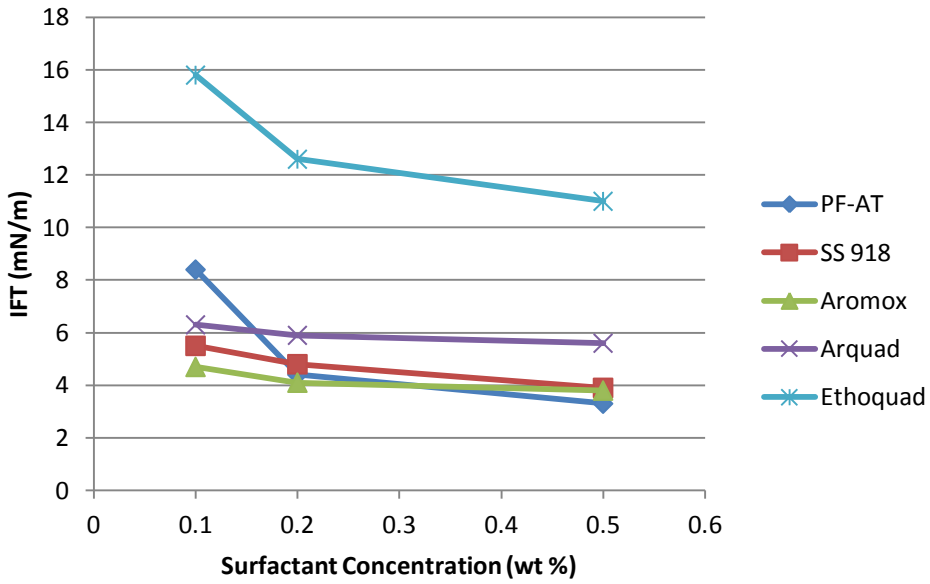

Fig. 9: Variation of surface tension with surfactant concentration between oil and different surfactant solutions in DI water

To study the IFT behavior of the surfactants in the presence of salts, the surfactant solutions were now prepared in formation brine. It was noted that the fluoro-surfactant

PF-AT was not compatible with the brine; it came out of the solution and precipitated as a white foggy solid. The IFT behavior of other four surfactants has been shown in Fig. 10 and the values have been listed in Table 3. We noted that except for Ethoquad, the CMC value for all the other surfactants shifted to the left and it was about 0.1 wt% or 1000 ppm. The lowering of CMC in the presence of salts is an expected behavior for surfactants (Noll 1991).

Lighter phase: **Oil 13-25-101-5**

Heavier phase: **Surfactant solution in brine**

Table 3: Values of surface tension for different surfactant concentrations between oil and surfactant solutions in brine

Surfactant	SS-918	Aromox	Arquad	Ethoquad
Surf Conc.%	IFT mN/m	IFT mN/m	IFT mN/m	IFT mN/m
0.05	11	13.3	11	22.3
0.1	5.7	4.9	8.4	19.7
0.2	3.5	3.4	8.4	10.9
0.5	3.7	5.4	7.8	10.1

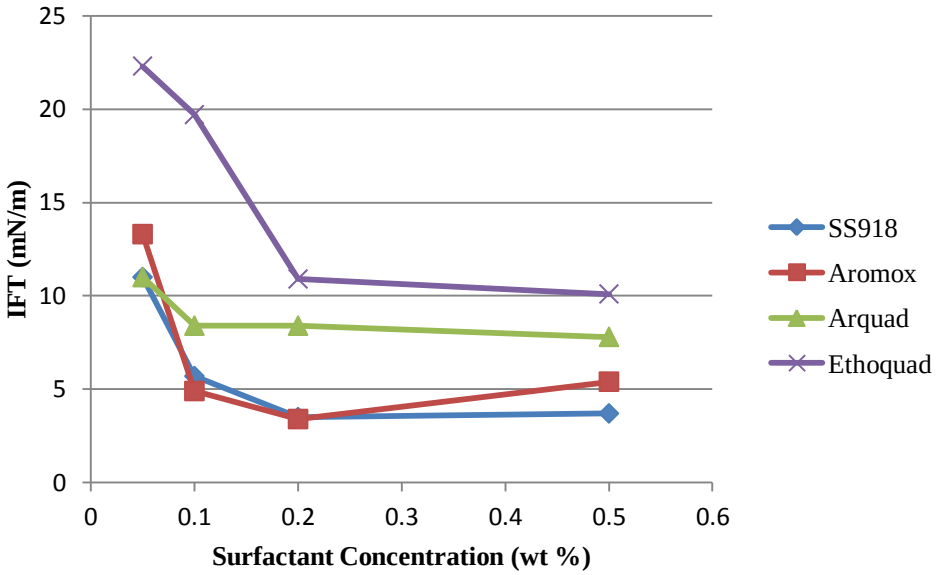

Fig. 10: Variation of surface tension with surfactant concentration between oil and different surfactant solutions in brine

To see the effect of xylene injection on the IFT values, the IFT was measured between surfactant solutions in brine and a 1:1 by volume mixture of oil and xylene. Very few studies have been done previously on this subject. For cationic surfactants the IFT values are supposed to decrease with decreasing organic content of the lighter phase (Sar Santosh and Nutan 2011). When xylene is added to the oil it will dissolve some of the oil and reduce the organic content and hence the IFT values are expected to be lower than the previous set of measurements. We note from Table 4 and Fig. 11 that the IFT values are lower than those shown in Table 3.

Lighter phase: **1:1 mixture (by volume) oil and xylene**

Heavier phase: **Surfactant solution in brine**

Table 4: Values of surface tension for different surfactant concentrations between 1:1 mixture of oil and xylene and surfactant solutions in brine

Surfactant	SS-918	Aromox	Arquad	Ethoquad
surf conc.%	IFT mN/m	IFT mN/m	IFT mN/m	IFT mN/m
0.01	3.1	2.3	3.9	8.3
0.05	2.8	1.5	3.7	7
0.1	3.3	2.9	4.9	7.5
0.2	2.8	4.9	5.4	7.6
0.5	2.6	5.4	6.1	7.8

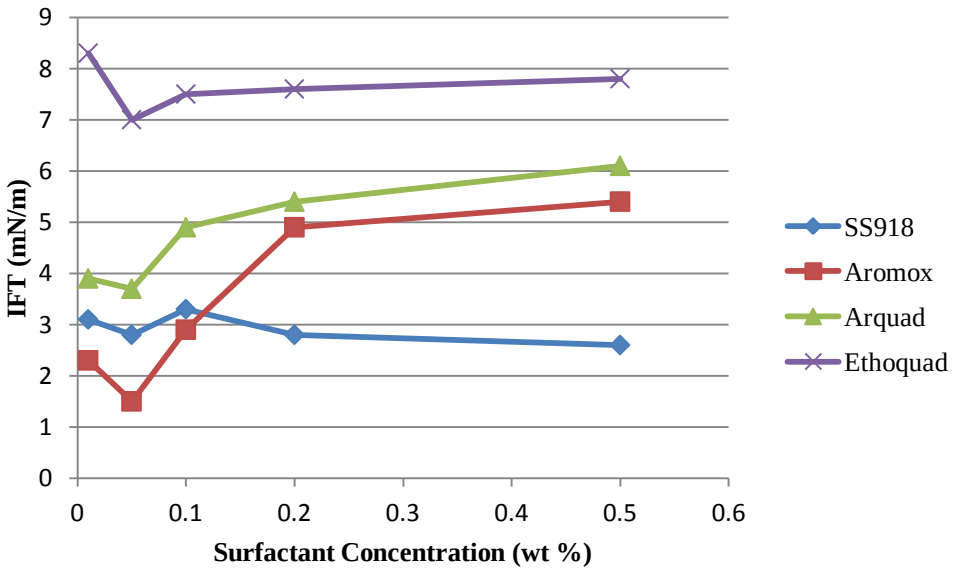

Fig. 11: Variation of surface tension with surfactant concentration between 1:1 mixture of oil and xylene, and different surfactant solutions in brine

The interfacial behavior of each surfactant for different combinations of lighter phase and heavier phase have been shown in the following pages. From Fig. 12 and Fig. 13 we

note that the average IFT values after crossing the CMC lie between 3 – 5 mN/m for both SS-918 and Aromox surfactants.

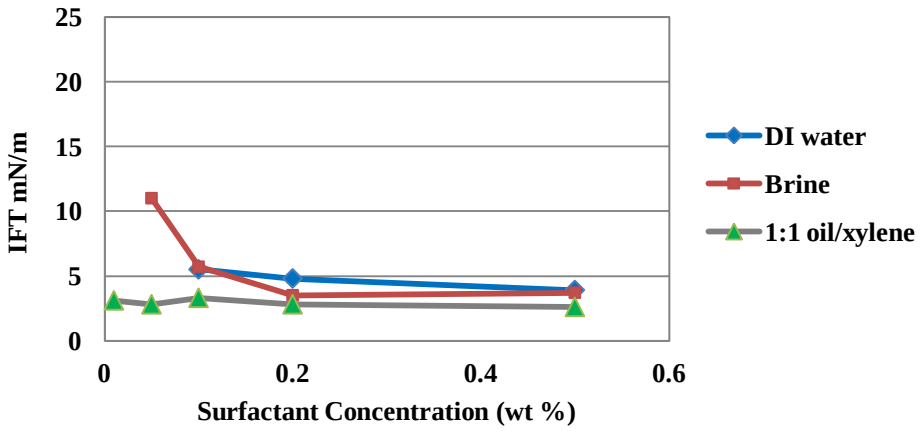

Fig. 12: IFT behavior of the surfactant SS-918 with different combinations of lighter phase and heavier phase

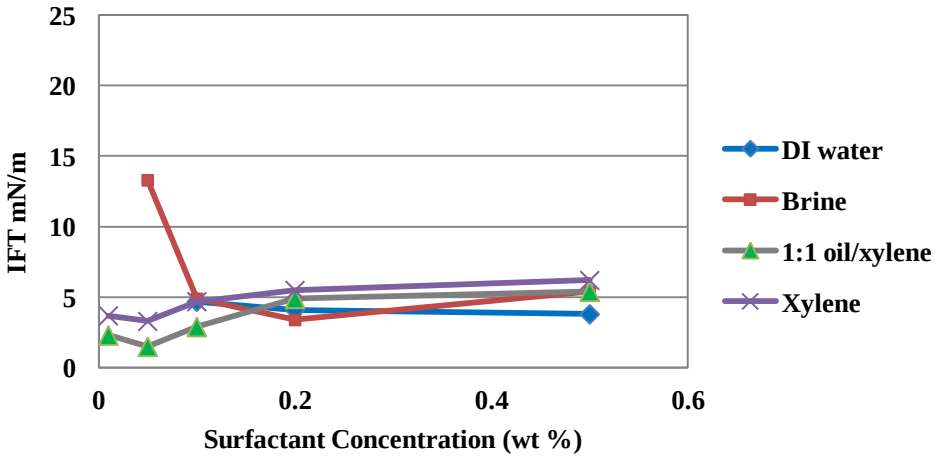

Fig. 13: IFT behavior of the surfactant Aromox with different combinations of lighter phase and heavier phase

Arquad and Ethoquad give higher IFT values compared to the other two surfactants. From Fig. 14 and Fig. 15 we note that the average IFT values after crossing the CMC lie between 6 – 8 mN/m for Arquad surfactant, where as they lie between 8 – 12 mN/m for Ethoquad surfactant.

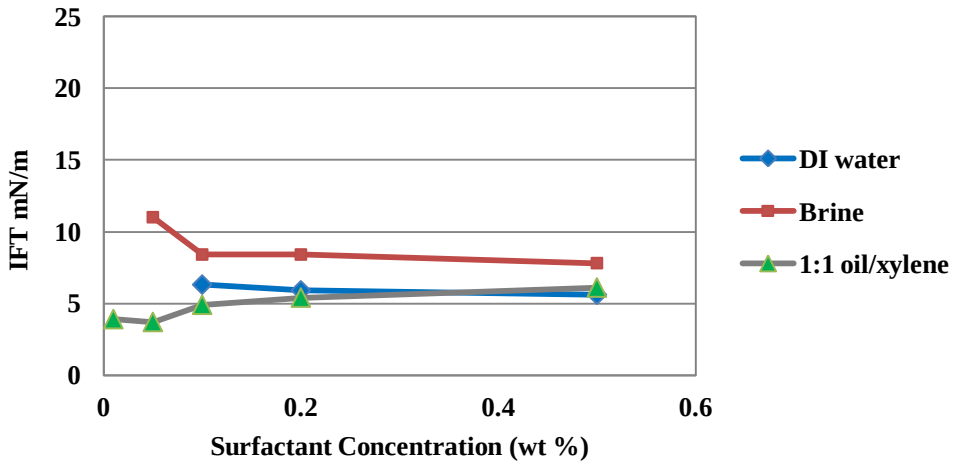

Fig. 14: IFT behavior of the surfactant Arquad with different combinations of lighter phase and heavier phase

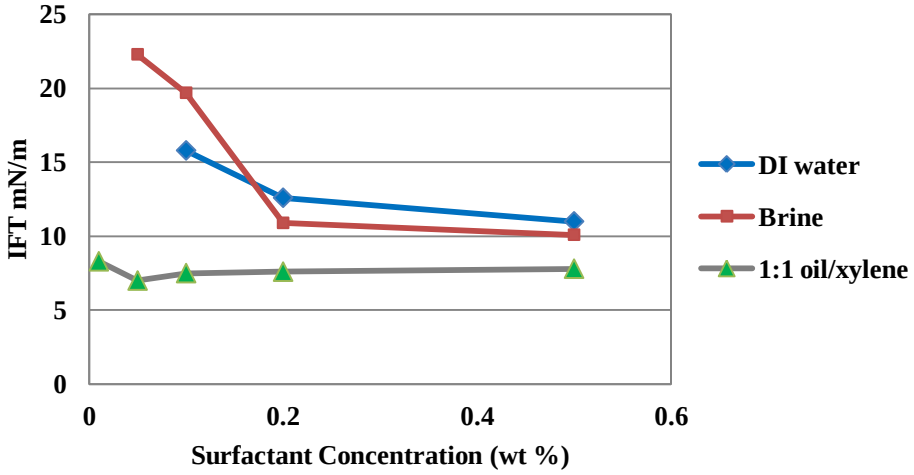

Fig. 15: IFT behavior of the surfactant Ethoquad with different combinations of lighter phase and heavier phase

3.3 Summary

Both Aromox and SS-918 surfactants give lower IFT values compared to the other two surfactants Arquad and Ethoquad. Aromox is a cationic surfactant whereas SS-918 is an amphoteric surfactant and for carbonate reservoirs the use of cationic surfactants is more favorable, this has been explained in the Wettability section, Chapter 4. So from the IFT measurements we conclude that Aromox is best suited for surfactant flooding of Pekisko formation.

4. WETTABILITY

4.1 Wettability and Surface Chemistry of Carbonate Rocks

Contact between two immiscible fluids and a solid surface and their mutual intermolecular interactions can be expressed by wettability. It is the preferential tendency of one of the fluids to adhere over the solid surface like a thin film. In a reservoir the fluid can be either water or oil and the solid surface is that of reservoir rock. Based on the interactions of water, oil and rock, the reservoir wettability may vary from strongly water-wet to strongly oil-wet. Some reservoir rocks exhibit neutral or intermediate wettability, where the rock does not have a preference to one of the reservoir fluids and the wettability is in between water-wet and oil-wet.

Some reservoirs exhibit fractional wettability, where few local areas are oil-wet while the others are water-wet. Fractional wettability occurs where reservoir rock has variable mineral composition and surface chemical composition. Fractional wettability is different from neutral wettability where all minerals present in the rocks have the same preference for being oil-wet or water-wet. In some reservoirs, the smaller pores are occupied by water and are water-wet while the larger pores are filled with oil and are oil-wet. This phenomenon occurs where oil with polar organic compounds enters a water wet formation saturated with brine.

Most of the reservoir rocks are originally water-wet since the sedimentary rocks are mainly formed in marine, fluvial or lacustrine environments. Their wettability changes to neutral, mixed, fractional or strongly oil-wet later during hydrocarbon migration into the porous medium. Few hydrocarbons contain surfactants in them which may alter the original wettability of the rock. For example, asphaltenes change the wettability from water-wet to oil-wet. (Macini and Mesini 2005).

Carbonatic reservoirs are mainly made up of calcium carbonate or calcite ($CaCO_3$) and calcium magnesium carbonate or dolomite ($CaMg(CO_3)_2$). Surface charge of these minerals is mainly determined by the oxygen atoms. Surface structure and surface charge of calcium carbonate dimers can be explained by the Hartree-Fock model(Mao and Siders 1997). This model divides the oxygen atoms into two types: non-bridging oxygen atoms, which bond with one calcium atom and bridging oxygen atoms, which bond with two calcium atoms. The structure which has the least molecular energy is known as the stabilized structure and according to this; the non-bridging oxygen atoms represent the edge of the calcite surface. At these non-bridging oxygen atoms hydrogen ion protonates which results in a net positive charge at the surface. Fig. 16 shows the most stable structure of calcium carbonate dimer.

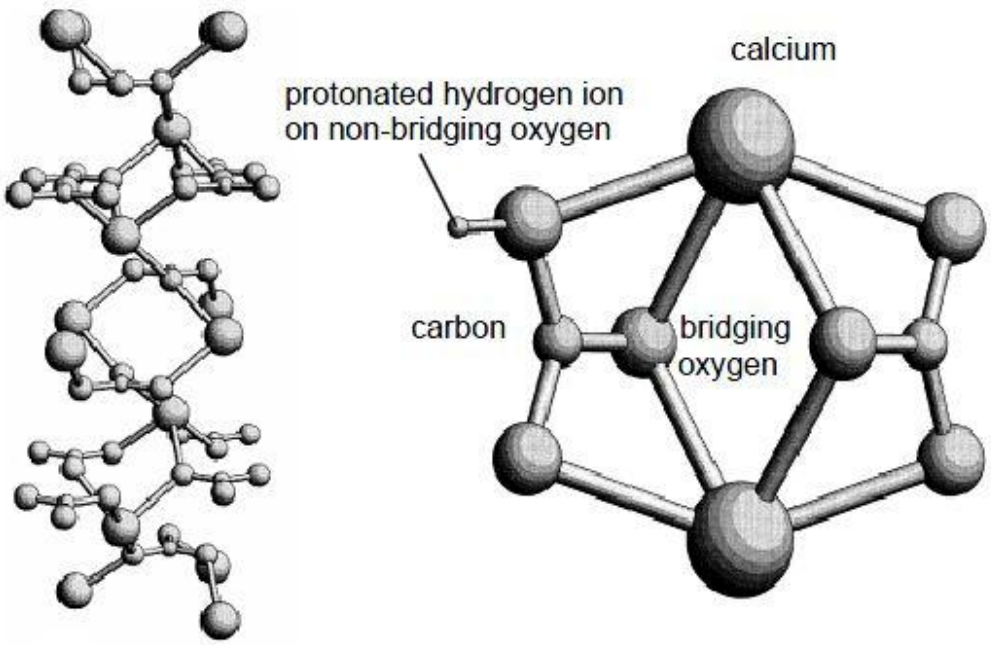

Fig. 16: Left: Three dimensional molecular lattice of calcite. Right: Surface structure of calcite (Bortolotti et al. 2010)

For a carbonate surface the point of zero charge (pzc) is around pH = 9 (Anderson 1986). So when pH < 9 the protonation of hydrogen ion dominates and hence there will be positive charge on the surface. As the pH value increases the OH^- ions concentration increases and the negative charge in the solution increases and the protonated hydrogen bonds are broken. This makes the surface negatively charged because of the un-bonded oxygen atoms on the carbonate surface (Bortolotti et al. 2010).

4.2 Wettability Reversal of Carbonate Rocks

Most of the carbonate rocks are originally water; the wettability is reversed to oil-wet during hydrocarbon migration. This can be explained by several mechanisms.

The natural crude oil generally contains some polar organic compounds like carboxylic acids. When this oil migrates into the water saturated rocks, the negatively charged carboxylic acids are attracted by the positively charged carbonate surface and they get adsorbed onto the surface and change its wettability by polar interaction mechanism (Bortolotti et al. 2010). Depending on the local thermodynamic conditions, the time taken to attain the wettability equilibrium varies for each pair of surface and adsorbed materials. In the laboratory conditions, the polar interaction mechanism can take from tens to hundreds of hours and up to geological times in natural geosystems. The polar interaction mechanism is slowed down by the connate water because the water film obstructs the direct bonding between rock surface and hydrocarbons. The film of connate water is completely removed at the equilibrium and the surface adsorption process is completed (Buckley et al. 1998).

Another mechanism to explain the wettability reversal in carbonate rocks is the precipitation of heavy compounds onto the grain surface. When reservoir conditions change, mainly pressure and temperature, the solvent properties of crude oil are affected. The dissolved heavy compounds in the crude oil can come out of solution and precipitate inside the pores. The polar parts of these heavy compounds are attracted to the carbonate surface due to the opposite charges and the non-polar part adheres to the oil phase, thus setting up an oil-wet surface (Bortolotti et al. 2010).

Oil-wet reservoirs are not favorable for oil production; their wettability needs to be changed to water-wet to improve the overall recovery factor. Also during well stimulation processes such as acidizing, the wettability needs to be changed to water-wet in order for the acid to come in contact with the reservoir rock and react with it.

Surfactant flooding is an effective way to reverse the wettability of reservoir rocks. Anionic surfactants are commonly used in surfactant flooding because they are resistant to retention time, stable and cheaper than cationic and non-ionic surfactants. But the use of anionic surfactants in carbonate reservoirs causes a large amount of surfactant retention in the formation because of the positively charged surface (Bortolotti et al. 2010). Cationic surfactants form ion pairs with the adsorbed negatively charged carboxylic acid groups and strips them off the rock surface, leaving the surface less oil-wet (Wu et al. 2006; Zhang et al. 2012).

4.3 Wettability Measurement

Wettability can be measured by several methods such as contact angle, Amott method and USBM method. Contact angle is the most direct method to measure the wettability of an uncontaminated solid surface immersed in a liquid.

The measurement called “Sessile drop method” is performed in a closed chamber where a rectangular piece of limestone is placed on a sample holder. The chamber is then sealed and it is filled with spent acid solution. Then an oil droplet is injected from the

bottom of the chamber, since the density of oil is less than that of water, so the droplet moves upward and sticks to the lower surface of the limestone piece. We take an image of this droplet and measure the contact angle from the image using the Drop Shape Analysis software by Kruss. A sample image has been shown in Fig. 17, which shows the profile of an oil droplet over limestone treated with 0.3 wt% Arquad surfactant solution and left in the chamber for 24 hours. The droplet has been left in the chamber for 24 hours because the contact angle changes with time as the oil/spent acid/surfactant treated rock surface reach equilibrium, this change becomes smaller as the time progresses (Golabi et al. 2012).

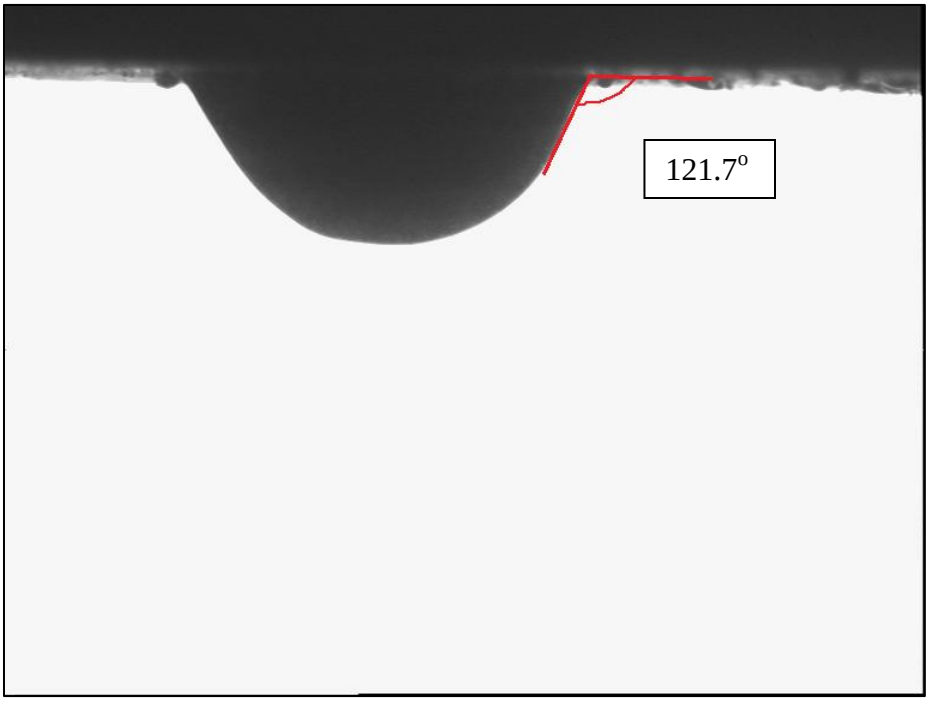

Fig. 17: Contact angle of an oil droplet over limestone treated with 0.3 wt % Arquad surfactant solution

4.3.1 Preparation of the Rock Sample and Spent Acid

The carbonate rock is prepared for contact angle measurement by simulating the flow sequence of liquids in the reservoir. We centrifuge the rock pieces at 6000 rpm for one hour to simulate the flow of liquids through it. First we centrifuge it in the formation brine, then in the formation oil. After this we age the rock in crude oil at 200^{o}F for 60 hours for making it oil-wet (Adejare et al. 2012). Finally after the rocks are oil-wet they are centrifuged in 0.3 wt% surfactant solution and ready for contact angle measurement.

A simulated spent acid solution was prepared in the lab by preparing 24 wt% solution of calcium chloride in de-ionized water and then the pH of the solution was adjusted to 4 – 5 by adding few drops of HCl(Chang et al. 2001; Nasr-El-Din et al. 2008).

The contact angle depends on three phases, the oil phase, the surrounding liquid phase (in this case spent HCl) and the surface of the carbonate rock. It also depends on the time; the initial value of the contact angle is high and decreases as the time progresses. This change becomes smaller and smaller with time. The measurements were done after 24 hours for each of the surfactants. We measured contact angle for carbonate rock treated with five different surfactants and the concentration of each of these surfactant solutions was 0.3 wt%. The repeatability of these measurements was ± 5 %. The results have been shown in Table 5 and have been plotted in Fig. 18 and Fig. 19. The error percent of each measurement has been plotted and shown in Fig. 20.

Table 5: Contact angle of oil droplet for calcite treated with different surfactants

Surfactant 0.3 wt %	Time (hrs)	Contact Angle 1st Measurement	Contact Angle 2nd Measurement	% error
Aromox	0	153.0	149.3	2.4
	12	103.5	108.6	-4.9
	24	87.0	91.7	-5.4
Arquad	0	159.2	154.2	3.1
	12	131.1	137.7	-5.1
	24	121.7	127.2	-4.5
Ethoquad	0	158.8	161.2	-1.5
	12	136.5	141.8	-3.9
	24	129.0	133.1	-3.2
PF-AT	0	143.2	148.3	-3.6
	12	126.6	129.3	-2.1
	24	121.1	124.5	-2.8
SS-918	0	141.4	148.9	-5.3
	12	111.3	114.9	-3.3
	24	101.2	103.9	-2.7

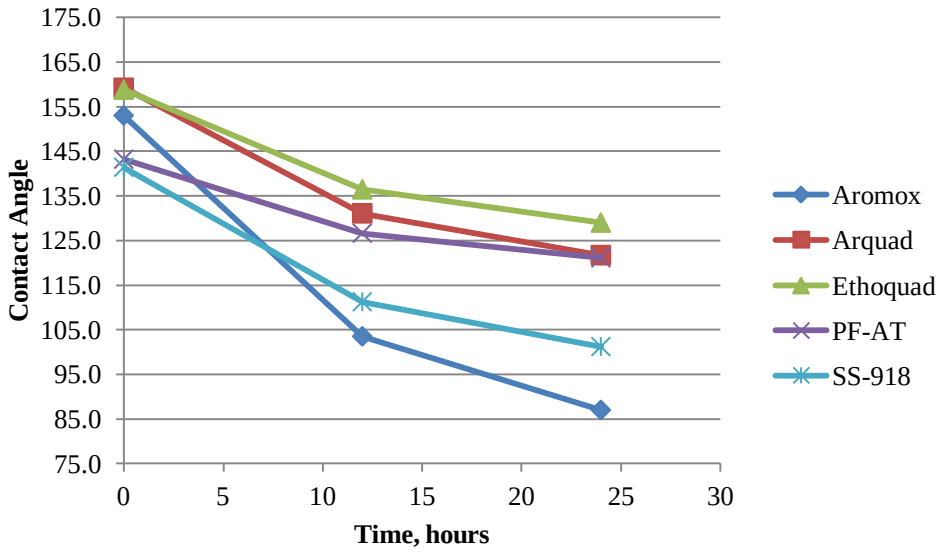

Fig. 18: Change of contact angle with time for different surfactants – measurement 1

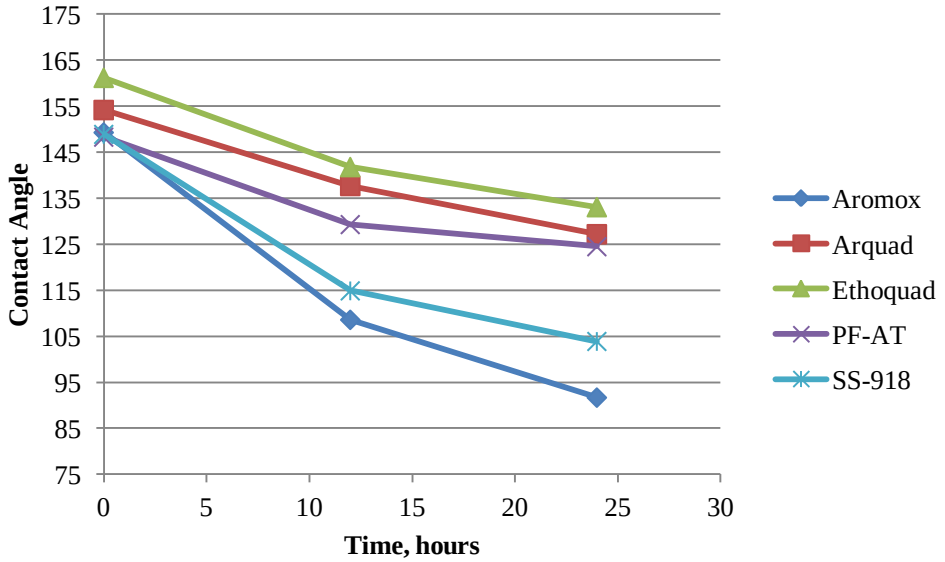

Fig. 19: Change of contact angle with time for different surfactants – measurement 2

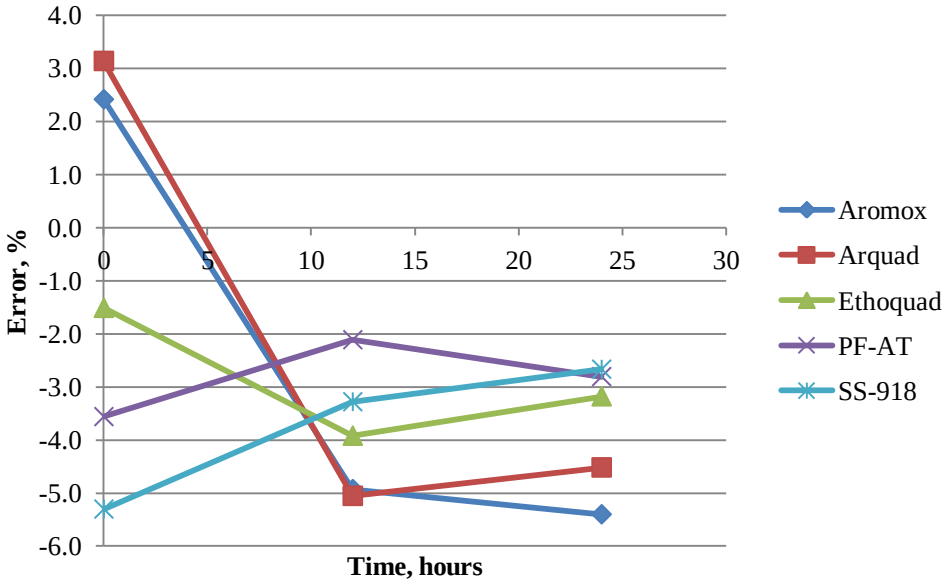

Fig. 20: Error margin between two sets of contact angle measurements

4.4 Summary

Among the five surfactants, we note that Aromox has achieved the lowest value of the contact angle (87^{o}), in other words it was most effective in changing the wettability of the rock from oil-wet to water-wet. Although the contact angle values achieved by SS-918 (101.2^{o}) are close to those of Aromox, but the latter being a cationic surfactant it is more effective for wettability reversal in carbonate reservoirs as explained earlier in section 4.2.

5. CORE FLOOD EXPERIMENTS

Core flood experiments are conducted to simulate the field conditions and injection sequences in the lab. In the present work, we tried to simulate the carbonate acidizing job to be conducted in the Pekisko formation, Canada. The formation is made up of limestone and it is strongly oil-wet. Conventional acidizing job with a surfactant pre-flush is not effective for this formation. We propose the use of an organic solvent which can remove the layer of oil that has formed on the rock surface around the wellbore so that subsequent acidizing job with a surfactant pre-flush can be effective.

Several organic solvents have been used in the past to dissolve the organic precipitates such as paraffin, wax and other heavy oils (Boswood and Kreh 2011; Newberry and Barker 1985). These solvents include n-heptane, xylene, toluene, chlorinated hydrocarbons (carbon tetrachloride) and carbon disulfide. The chlorinated hydrocarbons are good solvents, but have been banned, even in small quantities, because of damage to refinery catalysts. Carbon disulfide is extremely good paraffin solvent, but has such a low flash point as to be a major hazard. So the types of solvents most commonly used are xylene and toluene.

(Boswood and Kreh 2011) compared xylene and fully miscible micellar acidizing solvents for dissolving paraffin wax and determined that the latter was more effective,

because xylene is lighter than HCl, it separates and floats on the top. This is not effective as it should be the leading edge to dissolve the paraffin and make room for the acid to penetrate. But this problem can be overcome by doing a pre-flush with solvent (Newberry and Barker 1985).

(Barker et al. 2001) found that the dissolving power of solvents for paraffin wax was in the order xylene > n-heptane > arctic diesel. Also due to its easy availability and low price, we chose xylene as the solvent in all our experiments.

Xylene is an organic solvent and it will leave the rock oil-wet. After the pre-flush of xylene we propose to do a surfactant flooding to reverse the wettability of the formation rock to water-wet. We are going to use five surfactants for the pre-flush and compare the results of these core flood experiments.

5.1 Core Flood Setup

The core flood setup, described in Fig. 21 was constructed to simulate a matrix acidizing treatment. A back pressure of 1200 psi was applied to keep CO_2 in solution. Pressure transducers were connected to a computer monitor and recorded the pressure drop across the core during the experiments.

- We conducted six core flood experiments using 6" low permeability (k = 1.2 md) Indiana limestone cores.
- The core was first dried in the oven at 212^{o}F for 6 hours.

- It was saturated with formation brine.
- Oil was injected at 0.02 ml/min until the pressure drop across the core stabilizes. A very flow rate was used to inject the oil because of the low permeability of the core. A back pressure of 500 psi and an overburden pressure of 1000 psi were applied.
- For the first core flood experiment we did not inject xylene and surfactant solution; it was saturated with oil and then acidized after that.

For the other five core flood experiments the procedure is briefly described below.

- Xylene was injected at 2.5 ml/min through the oil saturated core to dissolve some of the oil present inside the core. Volume of xylene injected was 250 ml. An overburden pressure of 1000 psi and a back pressure of 400 psi were applied.
- 0.3 wt% surfactant solution prepared in de-ionized (DI) water was then injected at 1 ml/min. The amount of surfactant solution injected was 100 ml. An overburden pressure of 1000 psi and a back pressure of 400 psi were applied.
- 15 wt% HCl with 0.5 vol% corrosion inhibitor (CI-A supplied by Schlumberger) was then injected at 1 ml/min until break through. An overburden pressure of 1900 psi and a back pressure of 1200 psi were applied. It is important that a back pressure of about 1200 psi is applied while injecting HCl to make sure that the carbon dioxide produced by the reaction of HCl and calcium carbonate stays in the solution.

- The pressure drop profile during acid injection was recorded to exactly know the point at which breakthrough occurred.
- For the last core flood experiment we did not inject and surfactant solution. It was saturated with oil and then acidized after that.
- Finally we measured the oil permeability of the acidized cores and we found it to be 6000 – 8000 md which shows that the acidizing job was successful.

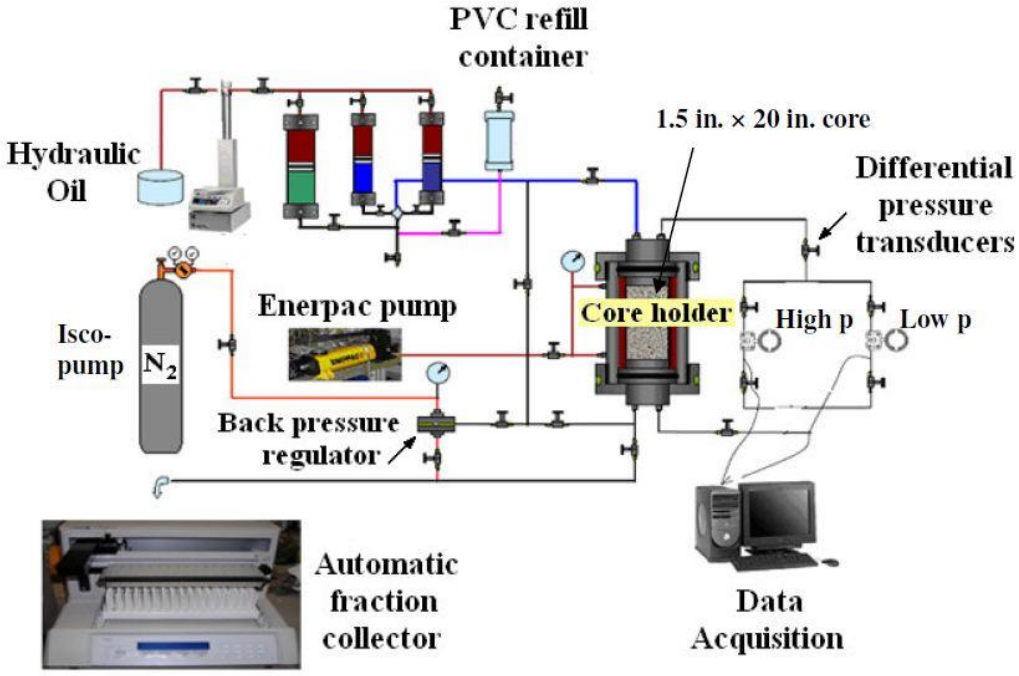

Fig. 21: Core flood set-up

5.2 Acidizing without Pre-flush of Xylene and Surfactant Solution

Shown in Fig. 22 are the effluent samples collected during injection of 15 wt % HCl through the oil saturated core.

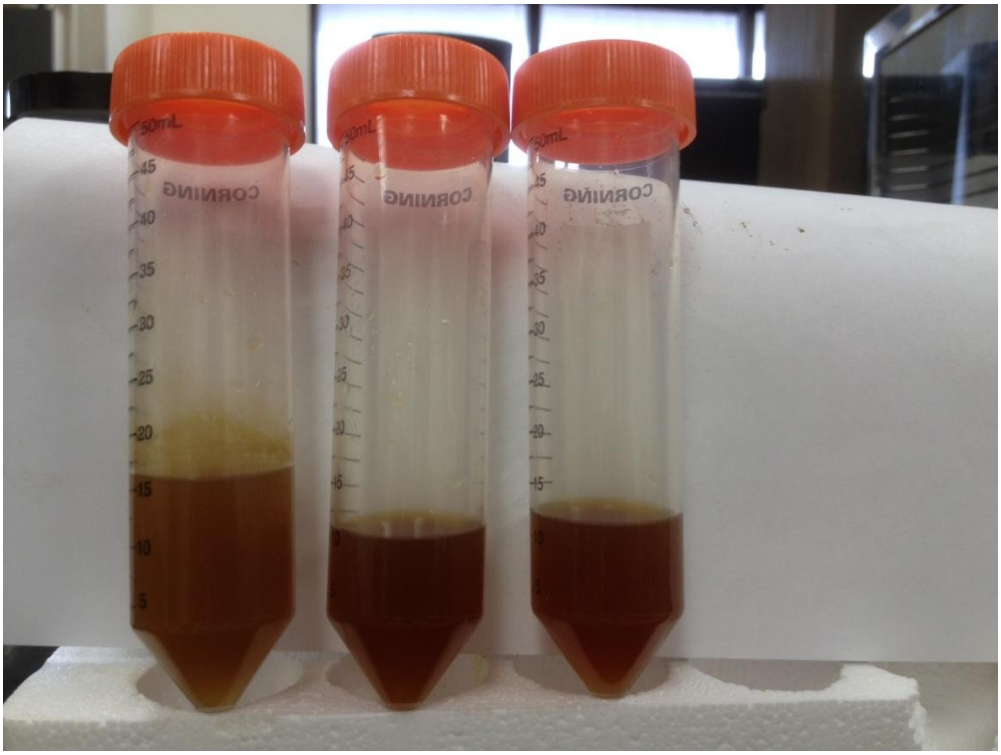

Fig. 22: No surfactant - Effluent samples collected during 15 wt % HCl injection

We can clearly see the wormhole formed after the acid breakthrough in Fig. 23 below.

Fig. 23: Core inlet and outlet after breakthrough

The point at which the pressure drop is almost zero indicates the breakthrough, which is after injection of 60 ml of HCl, as can be seen in Fig. 24 below.

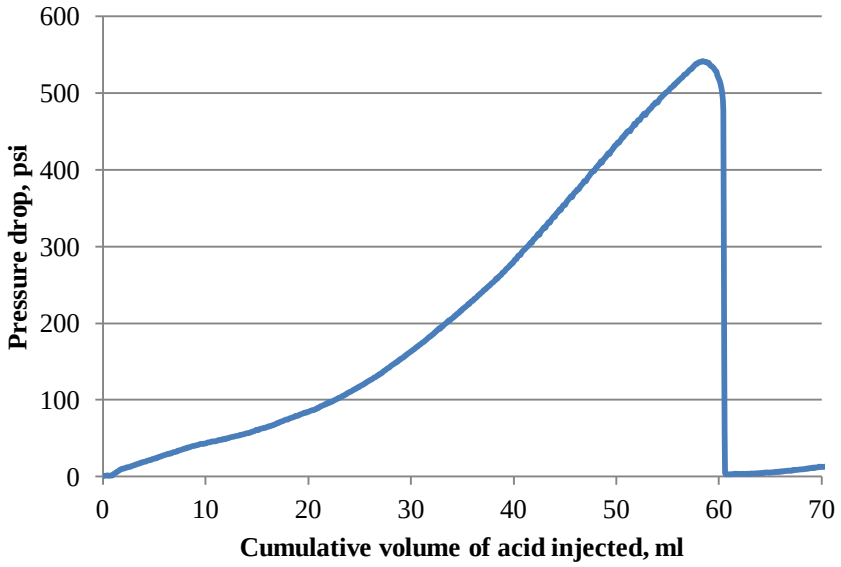

Fig. 24: No surfactant - Pressure drop profile during acid injection

5.3 Acidizing with a Pre-flush of SS-918 Surfactant

Shown in Fig. 25 through Fig. 27 are the effluent samples collected during xylene injection, 0.3 wt % SS-918 surfactant solution injection and 15 wt% HCl injection respectively.

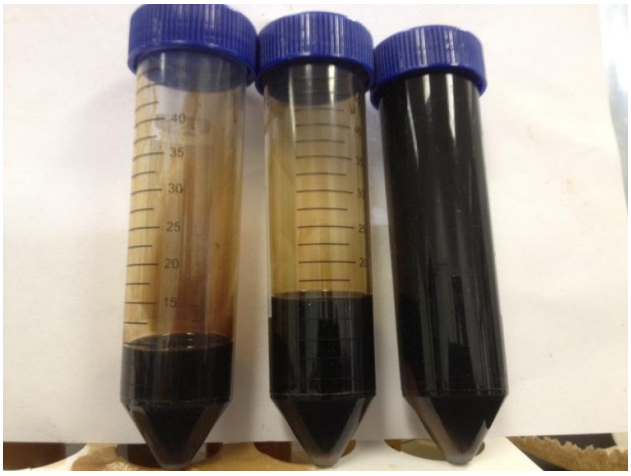

Fig. 25: SS-918 surfactant - Effluent samples collected during xylene injection

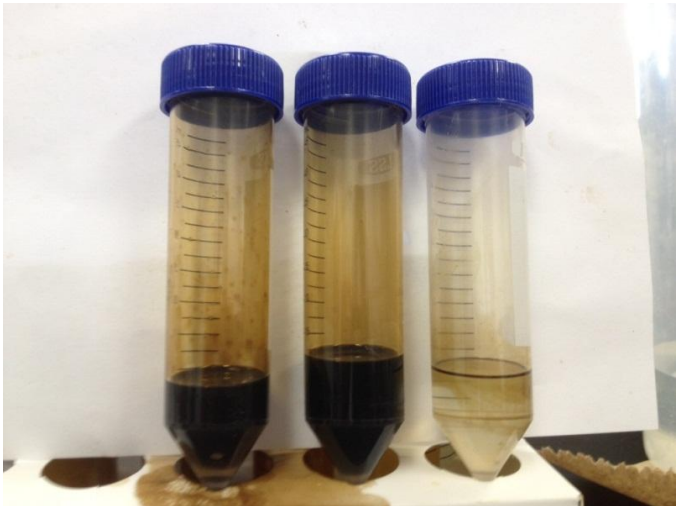

Fig. 26: Effluent samples collected during injection of 0.3 wt% SS-918 surfactant solution

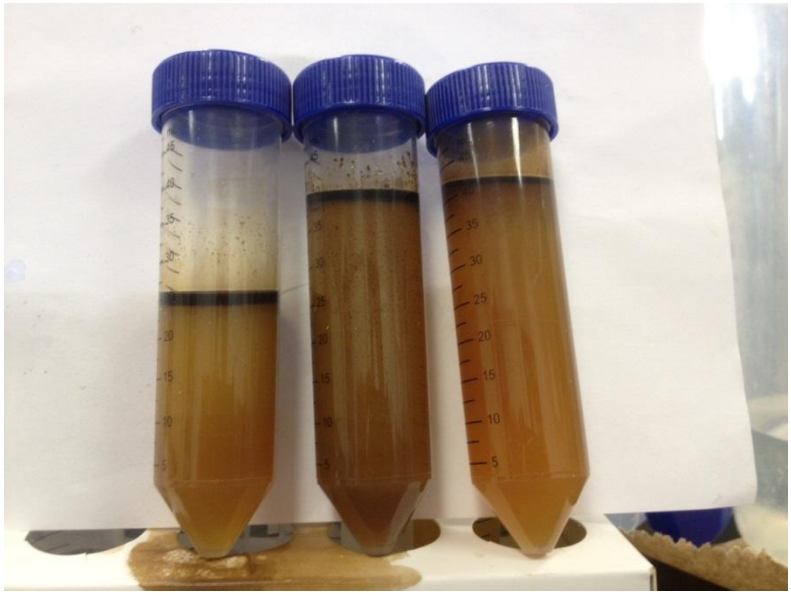

Fig. 27: SS-918 surfactant - Effluent samples collected during 15 wt% HCl injection

We can clearly see the wormhole formed after the acid breakthrough in Fig. 28 below.

Fig. 28: Core inlet and outlet after breakthrough

The point at which the pressure drop is almost zero indicates the breakthrough, which is after injection of 40 ml of HCl, as can be seen in Fig. 29 below.

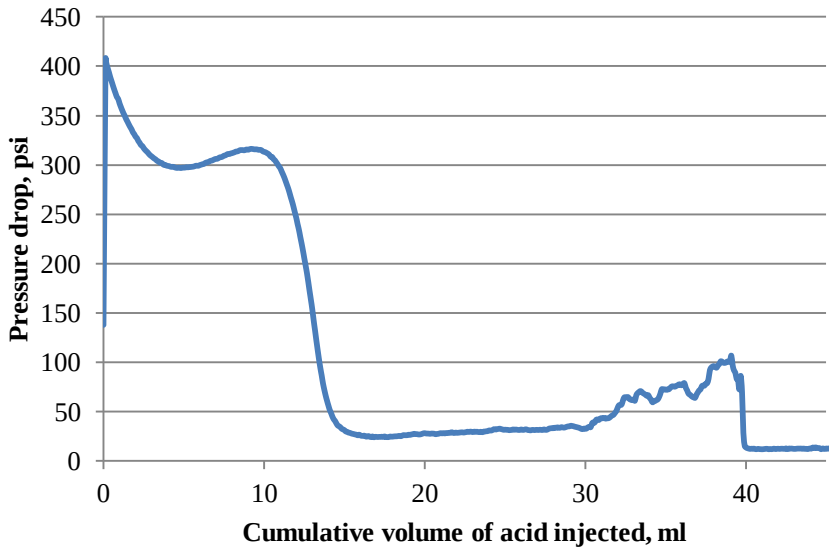

Fig. 29: SS-918 surfactant - Pressure drop profile during acid injection

5.4 Acidizing with a Pre-flush of Aromox Surfactant

Shown in

Fig. 30 through Fig. 32 are the effluent samples collected during xylene injection, 0.3 wt % Aromox surfactant solution injection and 15 wt% HCl injection, respectively.

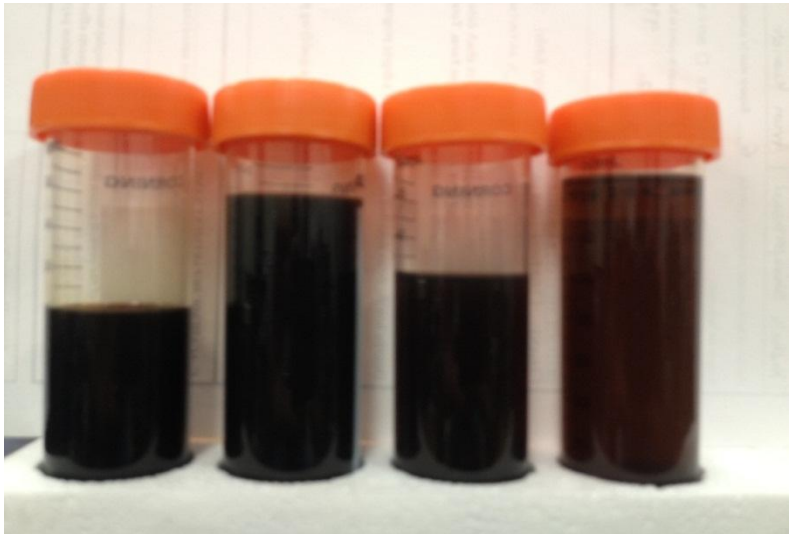

Fig. 30: Aromox surfactant - Effluent samples collected during xylene injection

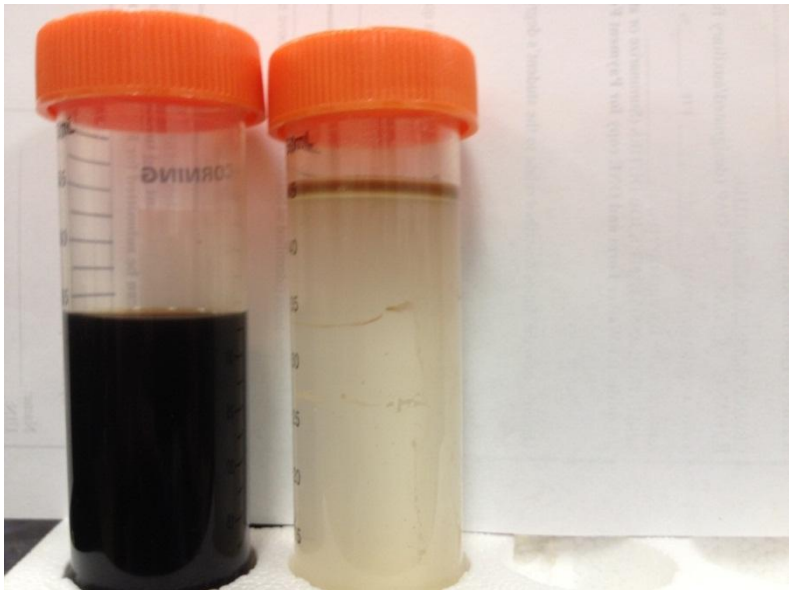

Fig. 31: Effluent samples collected during injection of 0.3 wt% Aromox surfactant solution

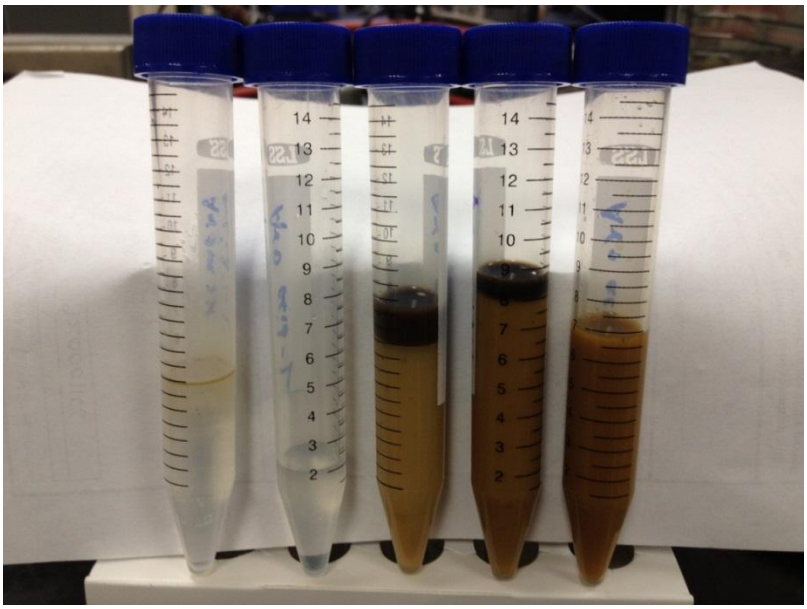

Fig. 32: Aromox surfactant - Effluent samples collected during 15wt % HCl injection

We can clearly see the wormhole formed after the acid breakthrough in Fig. 33 below.

Inlet Outlet

Fig. 33: Core inlet and outlet after breakthrough

The point at which the pressure drop is almost zero indicates the breakthrough, which is after injection of 25 ml of HCl, as can be seen in Fig. 34 below.

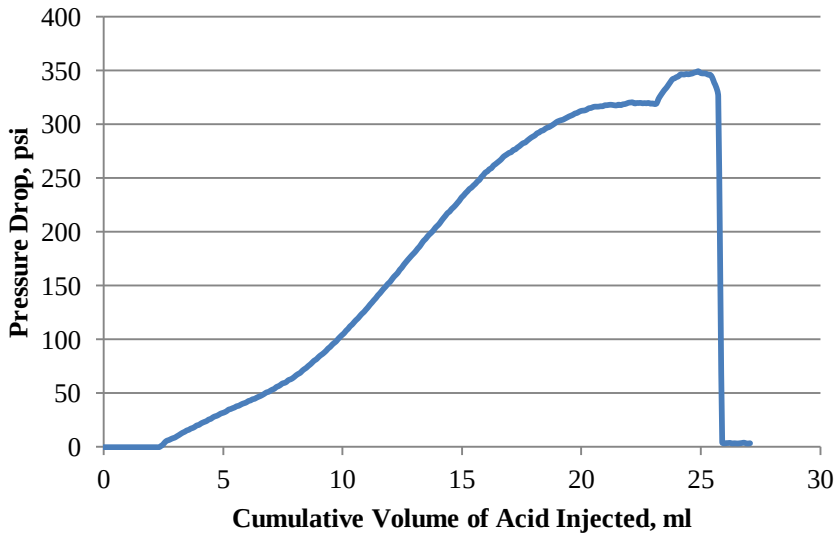

Fig. 34: Aromox surfactant - Pressure drop profile during 15 wt % HCl injection

5.5 Acidizing with a Pre-flush of Arquad Surfactant

Shown in Fig. 35 through Fig. 37 are the effluent samples collected during xylene injection, 0.3 wt % Arquad surfactant solution injection and 15 wt% HCl injection, respectively.

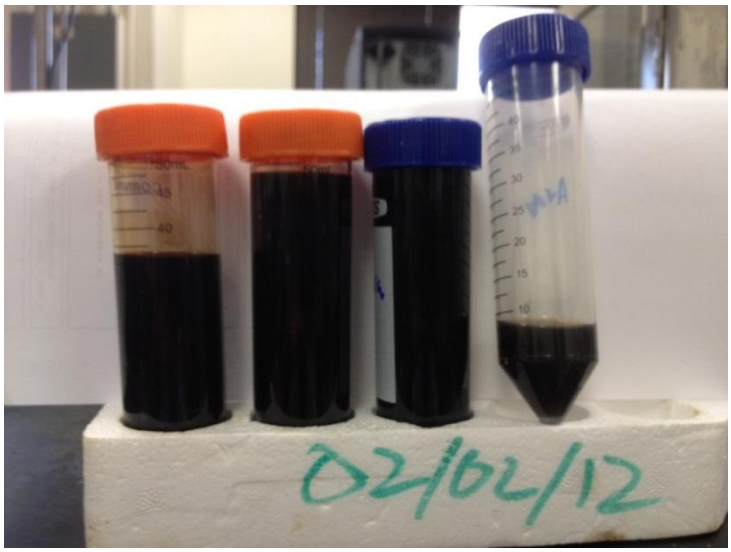

Fig. 35: Arquad surfactant - Effluent samples collected during xylene injection

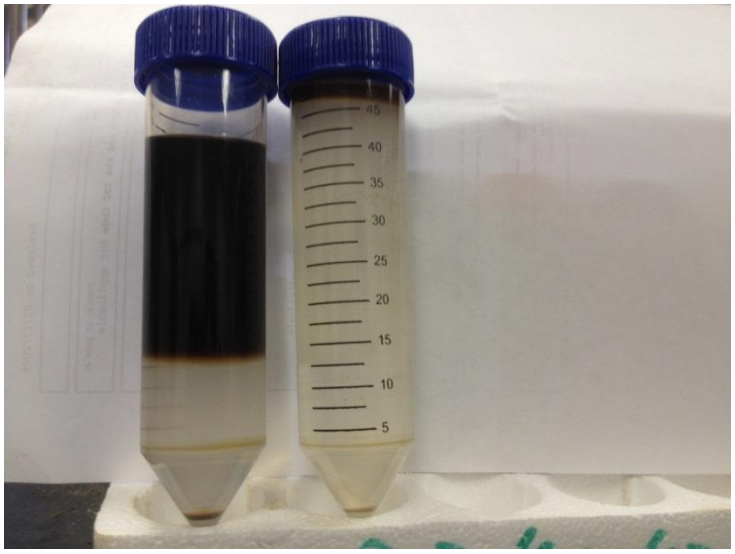

Fig. 36: Effluent samples collected during injection of 0.3 wt% Arquad surfactant solution

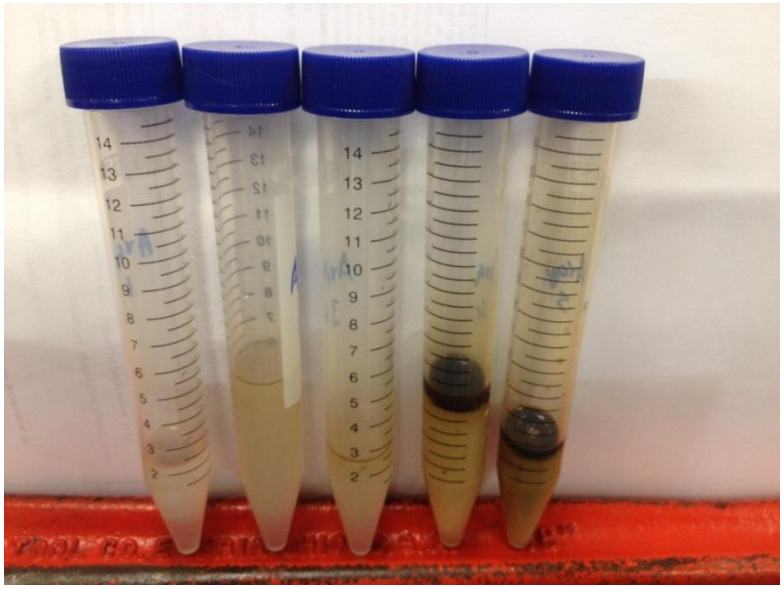

Fig. 37: Arquad surfactant - Effluent samples collected during 15 wt% HCl injection

We can clearly see the wormhole formed after the acid breakthrough in Fig. 38 below.

Fig. 38: Core inlet and outlet after breakthrough

The point at which the pressure drop is almost zero indicates the breakthrough, which is after injection of 45 ml of HCl, as can be seen in Fig. 39 below.

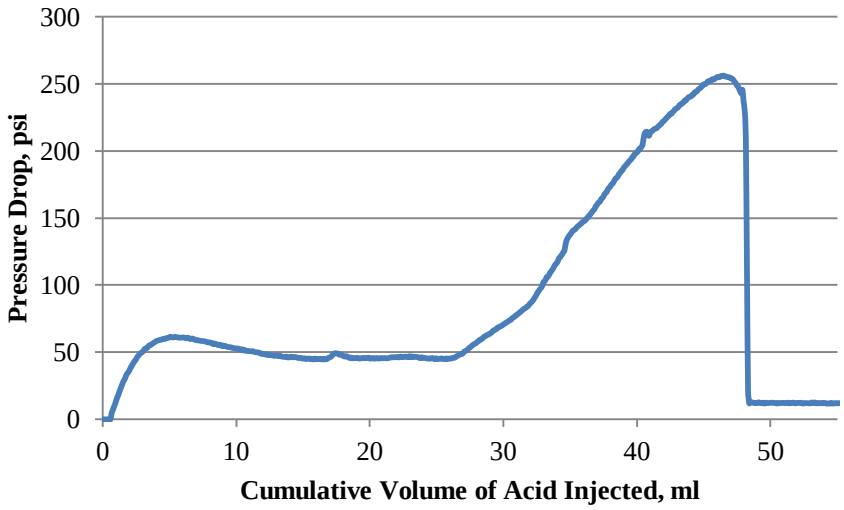

Fig. 39: Arquad surfactant - Pressured drop profile during 15 wt % HCl injection

5.6 Acidizing with a Pre-flush of Ethoquad Surfactant

Shown in Fig. 40 through Fig. 42 are the effluent samples collected during xylene injection, 0.3 wt % Arquad surfactant solution injection and 15 wt % HCl injection, respectively.

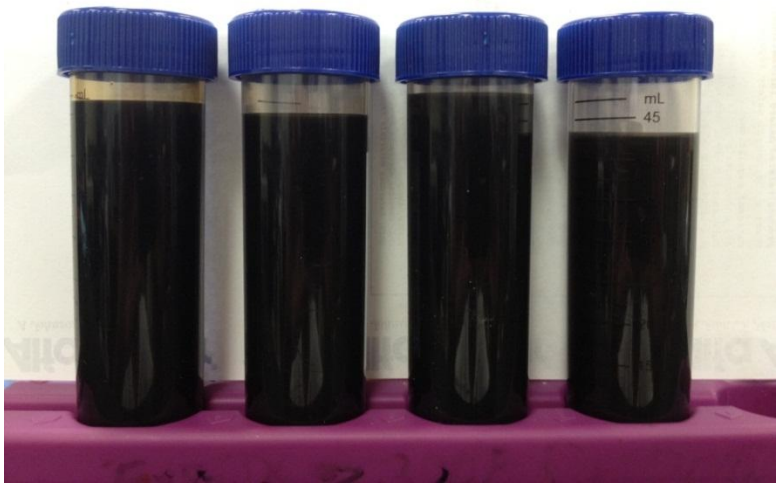

Fig. 40: Ethoquad surfactant - Effluent samples collected during xylene injection

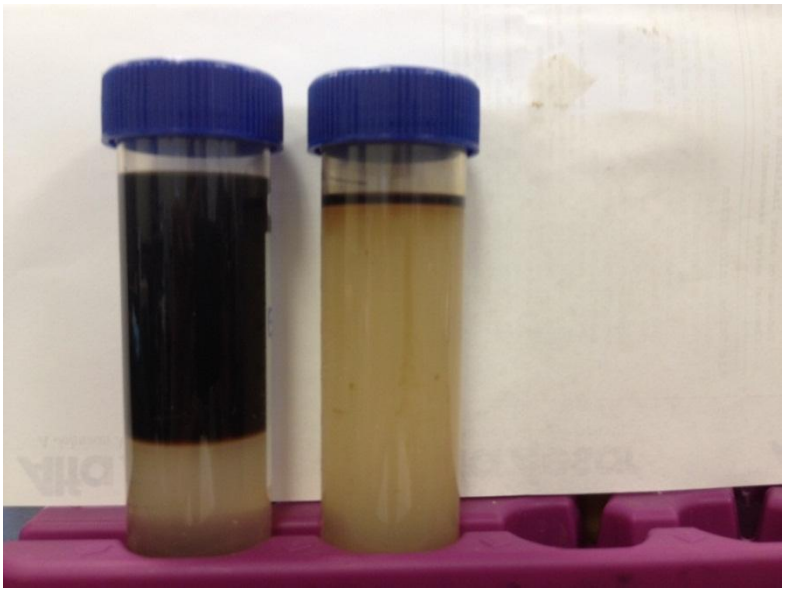
Fig. 41: Effluent samples collected during injection of 0.3 wt% Ethoquad surfactant solution

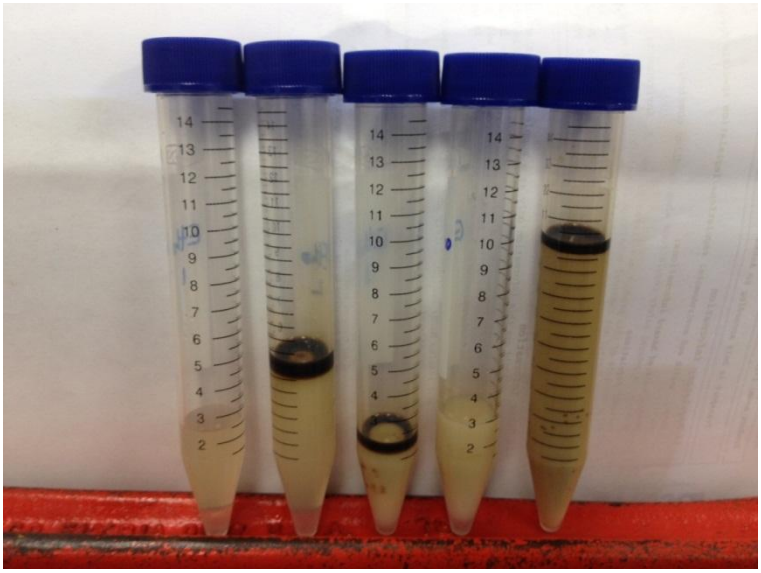

Fig. 42: Ethoquad surfactant - Effluent samples collected during 15 wt% HCl injection

We can clearly see the wormhole formed after the acid breakthrough in Fig. 43 below

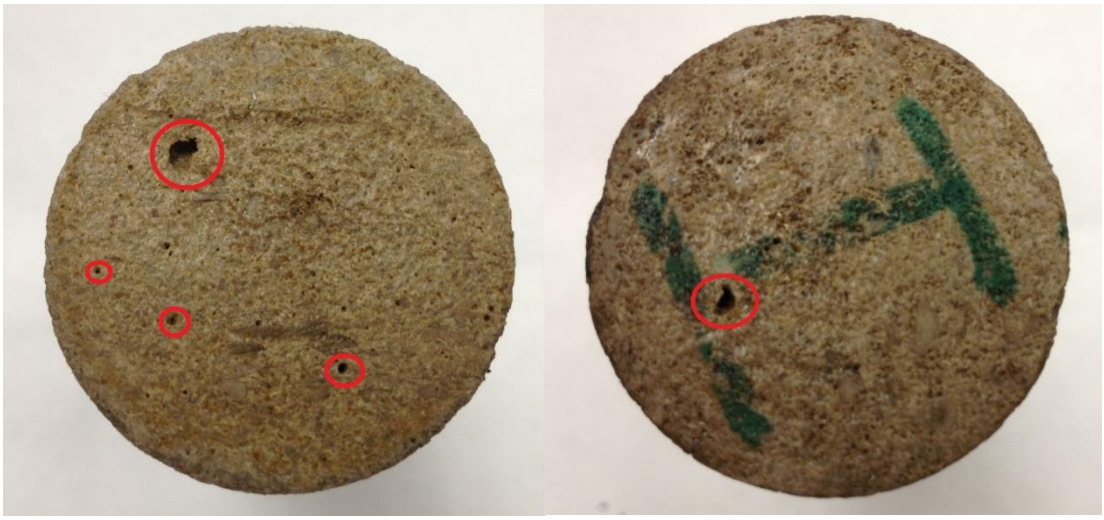

Fig. 43: Core inlet and outlet after breakthrough

The point at which the pressure drop is almost zero indicates the breakthrough, which is after injection of 32 ml of HCl, as can be seen in Fig. 44 below.

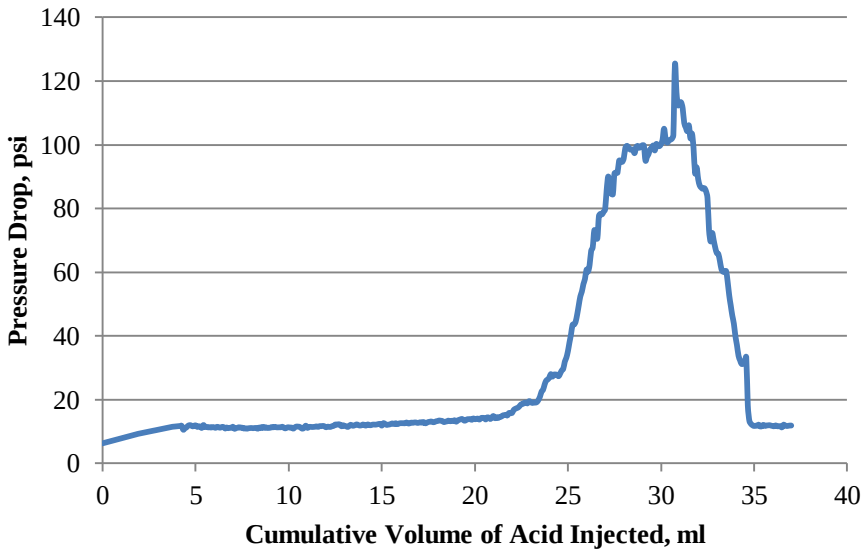

Fig. 44: Ethoquad surfactant - Pressured drop profile during 15 wt % HCl injection

5.7 Acidizing with a Pre-flush of PF-AT Surfactant

Shown in Fig. 45 through Fig. 47 are the effluent samples collected during xylene injection, 0.3 wt % Arquad surfactant solution injection and 15 wt% HCl injection, respectively.

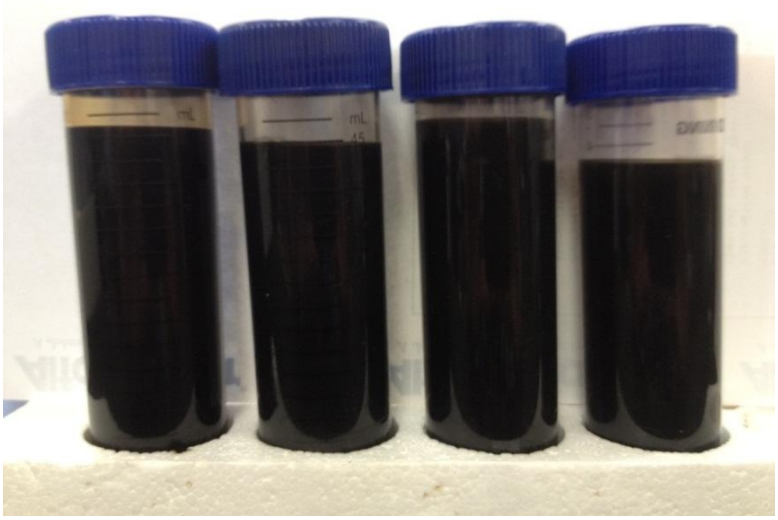

Fig. 45: PF-AT surfactant - Effluent samples collected during xylene injection

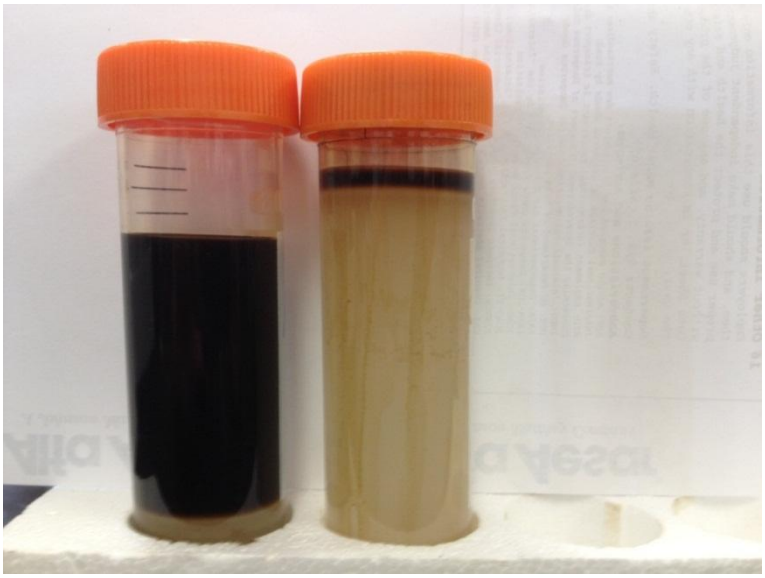

Fig. 46: Effluent samples collected during injection of 0.3 wt% PF-AT surfactant solution

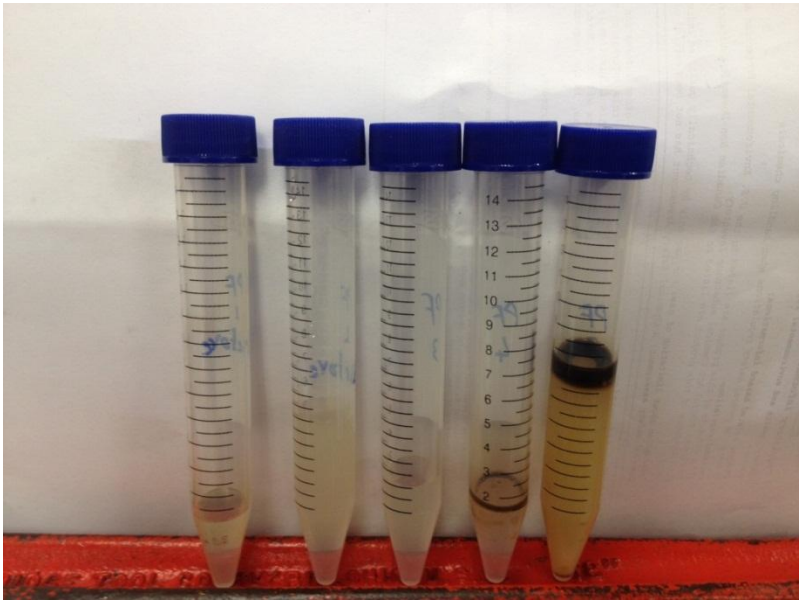

Fig. 47: PF-AT surfactant - Effluent samples collected during 15 wt% HCl injection

We can clearly see the wormhole formed after the acid breakthrough in Fig. 48 below.

Fig. 48: Core inlet and outlet after breakthrough

The point at which the pressure drop is almost zero indicates the breakthrough, which is after injection of 36 ml of HCl, as can be seen in Fig. 49 below.

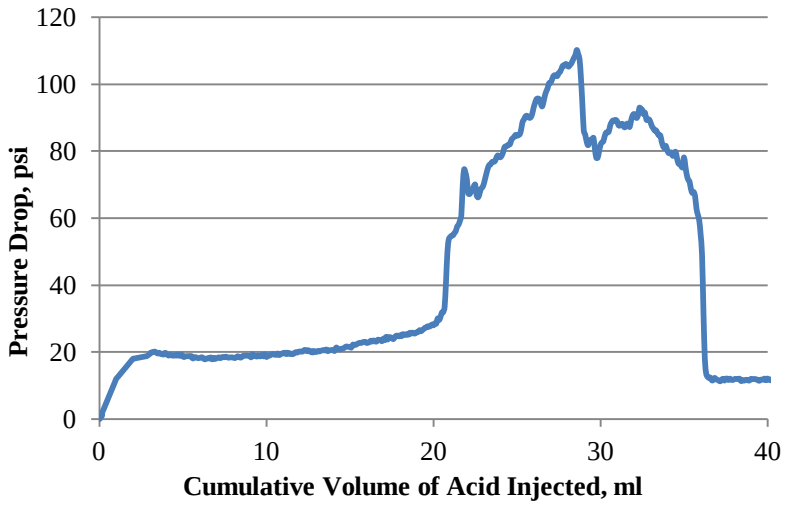

Fig. 49: PF-AT surfactant - Pressured drop profile during 15 wt% HCl injection

5.8 Summary of Core Flood Results

Shown in Table 6 is a summary of the results of the core flood experiments:

Table 6: Volume of acid consumed to reach breakthrough for different surfactant pre-flush

Surfactant	Volume of xylene ml	Volume of surfactant solution ml	Volume of acid to break through ml
No surfactant	0	0	60
SS-918	250	100	40
Aromox	250	100	25
Arquad	250	100	45
PF-AT	250	100	35
Ethoquad	250	100	32

As expected, we note that the amount of acid consumed to reach the breakthrough is least with a pre-flush of 0.3 wt% Aromox surfactant solution. This can be explained by the fact that it was able to achieve the lowest IFT values with all combinations of lighter phase and heavier phase fluids (explained in section 3.2) and also it was the most effective in changing the wettability of the rock from oil-wet to water wet.

5.9 Effluent Analysis

5.9.1 ICP-OES

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the concentration of Ca^{+} and Mg^{+} ions in the effluent samples (during acid injection) of core flood experiments. We noted that the samples mainly contained Ca ions and the Mg ions were negligible. This is expected because of the limestone core samples. Also, the presence of the Ca ions confirms that the reaction of HCl with the core was successful. The ICP results have been attached below.

5.9.2 pH Measurements

We titrated the effluent samples (during acid injection) of core flood experiments to measure the pH of the spent acid. pH of the effluent samples is measured to see that the reaction between HCl and carbonate has taken place and that the effluent sample pH is not close to zero initially. After breakthrough the acid flows freely through the wormhole formed and it will not react much with the rock, so the pH will be close to zero.

5.9.3 ICP and pH Measurements Results

Table 7 and Fig. 50 show the values of the Ca ion concentration and pH values of effluent samples collected with a pre-flush of Aromox surfactant.

Table 7: Aromox surfactant - Ca ion concentration and pH values of the effluent samples during acidizing

Samples	Ca mg/L	Mg mg/L	Ca orig. mg/L	H conc. (M)	pH	Volume ml
1	0.516	-0.111	1032		-	20
2	0.531	-0.161	1062		7.950	25
3	0.544	-0.173	1088		7.860	35
4	1.828	-0.161	3656	0.0672	1.173	45
5	19.41	-0.062	38820	1.452	-0.162	55

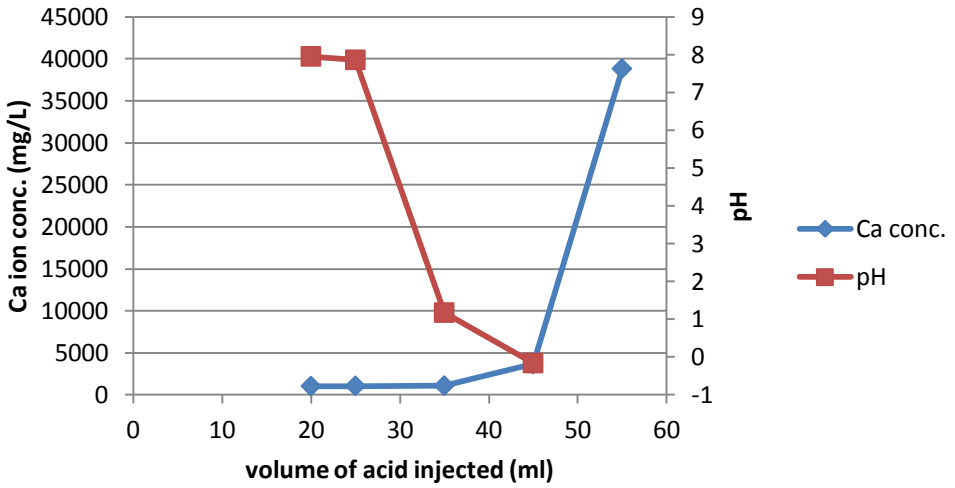

Fig. 50: Aromox surfactant – Variation of Ca ion concentration and pH values in the effluent samples during acidizing

Table 8 and Fig. 51 show the values of the Ca ion concentration and pH values of effluent samples collected with a pre-flush of Arquad surfactant.

Table 8: Arquad surfactant - Ca ion concentration and pH values of the effluent samples during acidizing

Samples	Ca mg/L	Mg mg/L	Ca orig. mg/L	H conc. (M)	pH	Volume
1	0.076	-0.175	152		-	20
2	0.015	-0.186	30		7.81	40
3	0.003	-0.179	6		7.85	50
4	-0.004	-0.184	0		7.8	60
5	1.476	-0.162	2952	0.0446	1.35	70

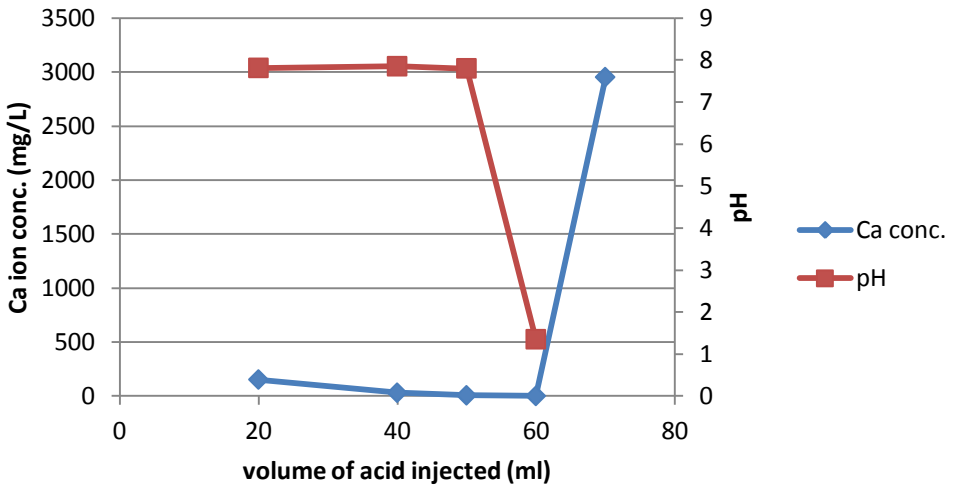

Fig. 51: Arquad surfactant – Variation of Ca ion concentration and pH values in the effluent samples during acidizing

Table 9 and Fig. 52 show the values of the Ca ion concentration and pH values of effluent samples collected with a pre-flush of Ethoquad surfactant.

Table 9: Ethoquad surfactant - Ca ion concentration and pH values of the effluent samples during acidizing

Samples	Ca mg/L	Mg mg/L	Ca orig. mg/L	H conc. (M)	pH	Volume
11	-0.0024	-0.176	0		7.44	20
12	-0.0032	-0.178	0		-	35
13	-0.019	-0.187	0		7.52	45
14	-0.029	-0.173	0		7.63	55
15	5.002	-0.143	10004	0.4406	0.356	65

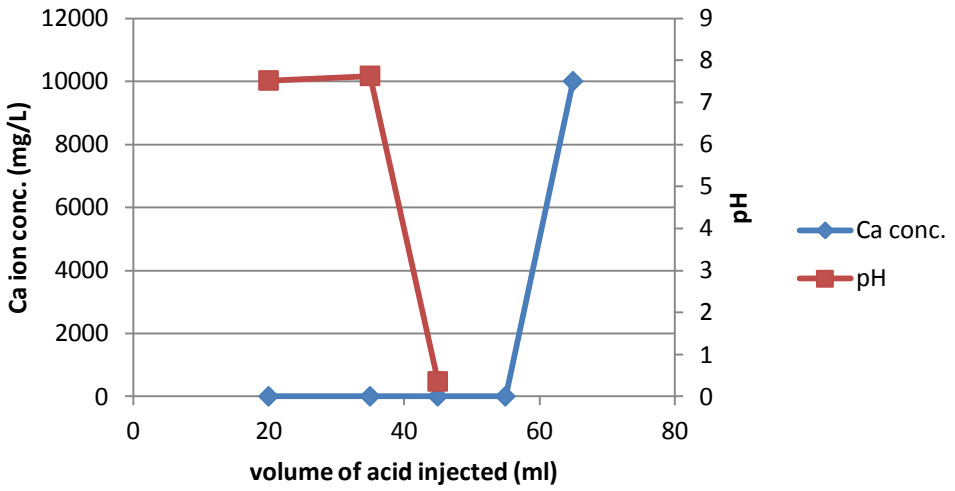

Fig. 52: Ethoquad surfactant – Variation of Ca ion concentration and pH values in the effluent samples during acidizing

Table 10 and Fig. 53 show the values of the Ca ion concentration and pH values of effluent samples collected with a pre-flush of Aromox surfactant.

Table 10: PF-AT surfactant - Ca ion concentration and pH values of the effluent samples during acidizing

Samples	Ca mg/L	Mg mg/L	Ca orig. mg/L	H conc. (M)	pH	Volume
16	0.21	-0.179	420		7.63	20
17	0.24	-0.169	480		7.67	35
18	7.168	-0.123	14336	0.2638	0.578	45
19	18.48	-0.068	36960	2.144	-0.331	55
20	11	-0.12	22000	2.944	-0.468	65

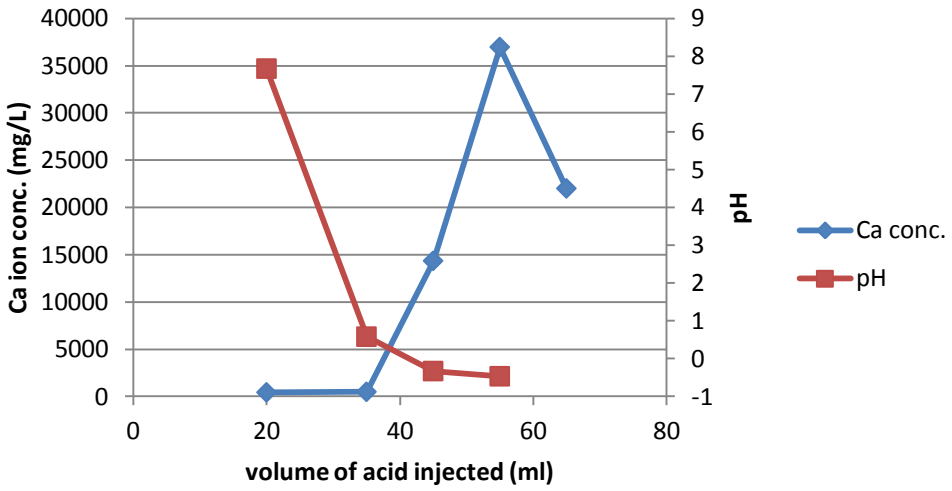

Fig. 53: PF-AT surfactant – Variation of Ca ion concentration and pH values in the effluent samples during acidizing

5.9.4 Summary of ICP-OES and pH Results

pH results of each effluent samples show that they have a value close to 7 initially, which is probably because of the surfactant solution coming out of the core at the beginning of acidizing and that value reduces close to zero at the end which indicates the formation of a wormhole where the acid would just flow freely without reacting with the rock.

ICP-OES results indicate that there are no magnesium ions in the solution which is expected because the core is mainly limestone as determined by XRF and XRD results in Chapter 2. The high Ca ion concentration indicates that the reaction of HCl with the core was successful.

6. CONCLUSIONS

The present work can be divided into two parts: selection of the appropriate surfactant that can attain low IFT values and changing the wettability of limestone formation from oil-wet to water and then simulating the acidizing job by conducting core flood experiments.

Selection of the surfactant was based on several tests:

- Compatibility of the surfactants with formation brine was tested. Some surfactants are not soluble in formation brines; the salts present in the brine will push the surfactant out of solution and precipitate them. We noted that the fluor-surfactant Polyfox AT (PF-AT) formed white foggy precipitate in the brine and this precipitate can cause formation damage.
- We conducted three types of interfacial tension (IFT) measurements for each surfactant: IFT between oil and 0.3 wt% surfactant solution prepared in DI water, IFT between oil and 0.3 wt% surfactant solution prepared in formation brine and IFT between 1:1 by volume mixture of oil and xylene and 0.3 wt% surfactant solution prepared in formation brine. Based on these three sets of measurements, we noted that the CMC of each surfactant in a particular set of measurement was almost the same but the lowest IFT values were attained by the surfactant Aromox.

- We conducted wettability measurements by contact angle method. The change of contact angle with time was measured for a surfactant concentration of 0.3 wt% and the contact angle values for each surfactant were compared. It was noted that Aromox surfactant was able to achieve the least contact angle value, in other words, it was most effective in changing the wettability of carbonate surface from strongly oil-wet to less oil-wet or water-wet.

After selection of Aromox as the most suitable surfactant for use in acidizing, we simulated the acidizing job by conducting core flood experiments. We conducted five core flood experiments each with a different surfactant pre-flush and one without any surfactant pre-flush and noted the amount of acid required to reach the breakthrough. We noted that a pre-flush of Aromox surfactant solution consumed the least amount of acid.

From IFT measurements, wettability measurements and core flood experiments, Aromox surfactant is the most suitable for achieving low IFT values and changing the wettability of the formation rock and aid in the carbonate matrix acidizing job.

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APPENDIX A

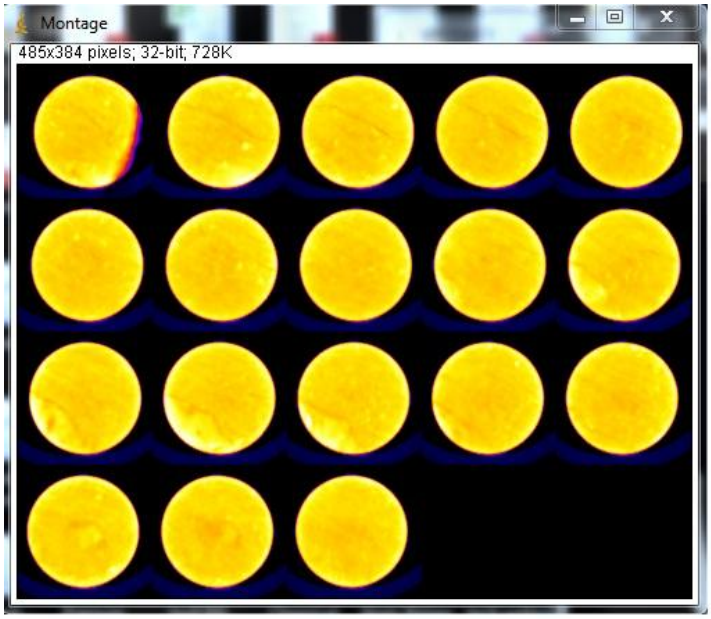


Figure: CT scan of the core #764.8

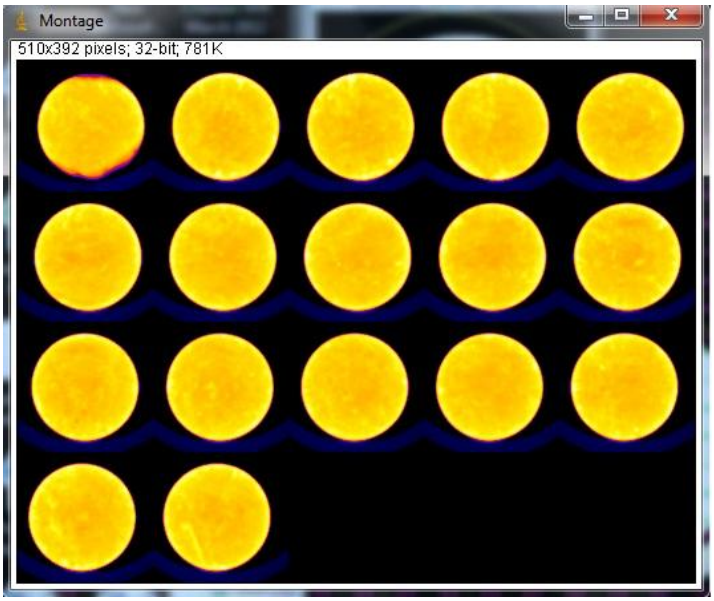


Figure: CT scan of the core #773.4

APPENDIX B

Table: Individual compounds and elements present in core sample 764.8

Compound	Concentration wt. %	Element	Concentration wt. %
$CaCO_3$	91.6	O	47.8
SiO_2	3.76	Ca	36.7
MgO	1.57	C	11
SO_3	1.04	Si	1.76
Al_2O_3	0.819	Mg	0.946
Cl	0.403	Al	0.434
Fe_2O_3	0.365	S	0.417
K_2O	0.226	Cl	0.403
TiO_2	0.0593	Fe	0.255
SrO	0.053	K	0.188
SnO_2	0.0135	Sr	0.0448
MnO	0.0116	Ti	0.0355
		Sn	0.0106

Table: Individual compounds and elements present in core sample 773.4

Compound	Concentration wt. %	Element	Concentration wt. %
$CaCO_3$	95.8	O	47.8
SiO_2	1.71	Ca	38.4
MgO	0.787	C	11.5
SO_3	0.652	Si	0.798
Cl	0.372	Mg	0.475
Al_2O_3	0.34	Cl	0.372
K_2O	0.127	S	0.261
Fe_2O_3	0.089	Al	0.18
SrO	0.0516	K	0.106
SnO_2	0.0128	Fe	0.0622
		Sr	0.0436
		Sn	0.0101

APPENDIX C

Table: Individual components of the oil sample 13-25-101-5

Compounds	13-25-101-5
	Mass %
Cyclohexane	5.28%
Cyclobutane, ethenyl-	5.51%
Cyclohexane, methyl-	9.11%
Toluene	3.58%
Cyclohexane, 1,3-dimethyl-	4.45%
Octene	4.14%
Cyclohexane, 1,1,3-trimeth	3.08%
o-Xylene	6.15%
Dodecane	2.11%
Tridecane	5.66%
Tetradecane	3.34%
Pentadecane	4.60%
Hexadecane	5.98%
Hexadecane, 2,6,11,15-tetr	2.90%
Hexadecane, 2,6,10,14-tetr	5.41%
Pentadecane, 2, 6, 10 tri	3.04%
Heptadecane	4.95%
Pentadecane, 2, 6, 10, 14-tetr	3.22%
Nonadecane	2.65%
Eicosane	2.76%
Heneicosane	2.44%
Docosane	2.81%
Tricosane	2.27%
Tetracosane	2.58%
Pentacosane	2.01%
Aromatic	**37.17%**
Aliphatic	**62.83%**

TAN report of the oil sample 13-25-102-5

Determination

Method	TAN with Blank Subtraction-DET U Manual
Method saving date	2011-09-07 08:24:35 UTC-5
Method version	5
Method state	original
Determination start	2011-11-11 15:42:41 UTC-6
Determination state	original
Determination version	1
Run number	3
User (full name)	
User (short name)	junli.chen

Sample data

Sample Name		
Sample size	9.9785	g

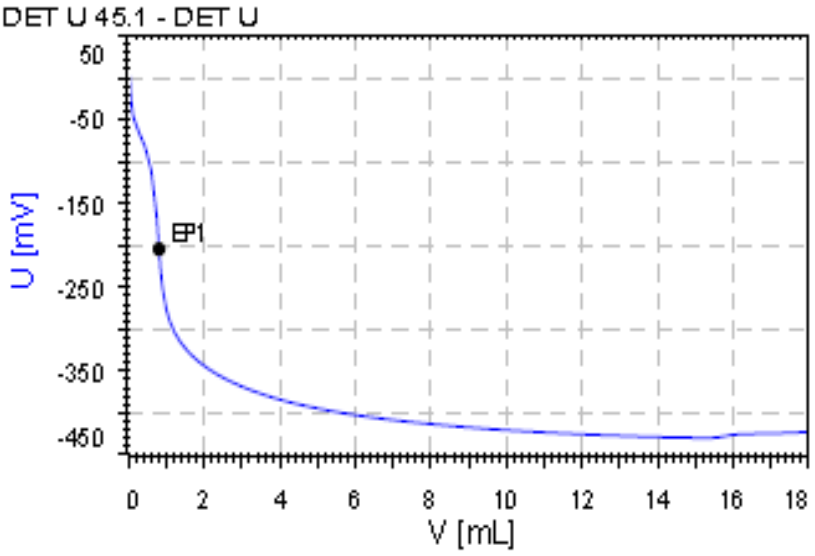
End points

DET U DET U 45.1

EP1	-204.5	mV	0.8021	mL

Results

TAN	0.4009	mg/g



TBN report of the oil sample 13-25-102-5

Determination

Method	TBN with Blank Subtraction-DET U Manual
Method saving date	2011-08-31 14:38:07 UTC-5
Method version	3
Method state	original
Determination start	2011-11-16 09:05:43 UTC-6
Determination state	modified
Determination version	2
Run number	1
User (full name)	
User (short name)	junli.chen

Sample data

ID1		
Sample size	9.6853	g

End points

DET U DET U.1

EP1	474.3	mV	4.5718	mL

Results

Base number	2.62	mg/g